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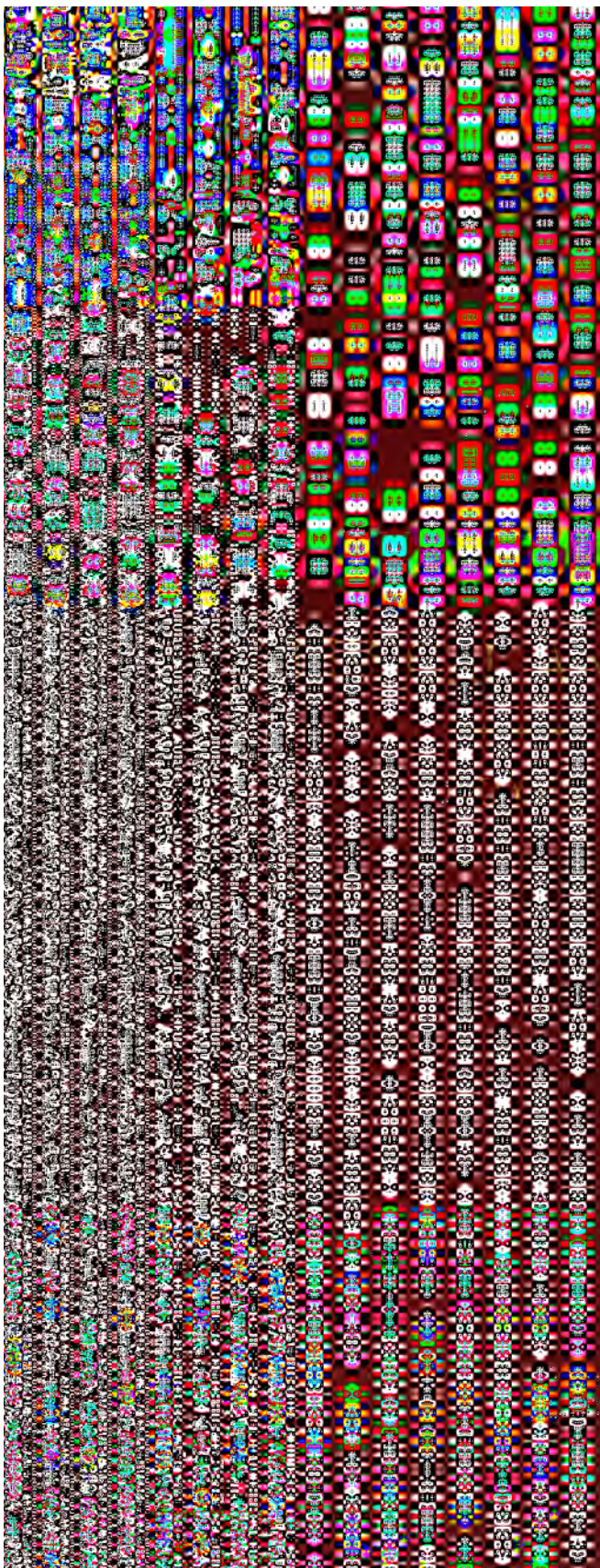
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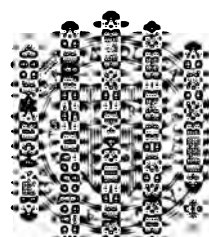


# IVE ANALYSIS

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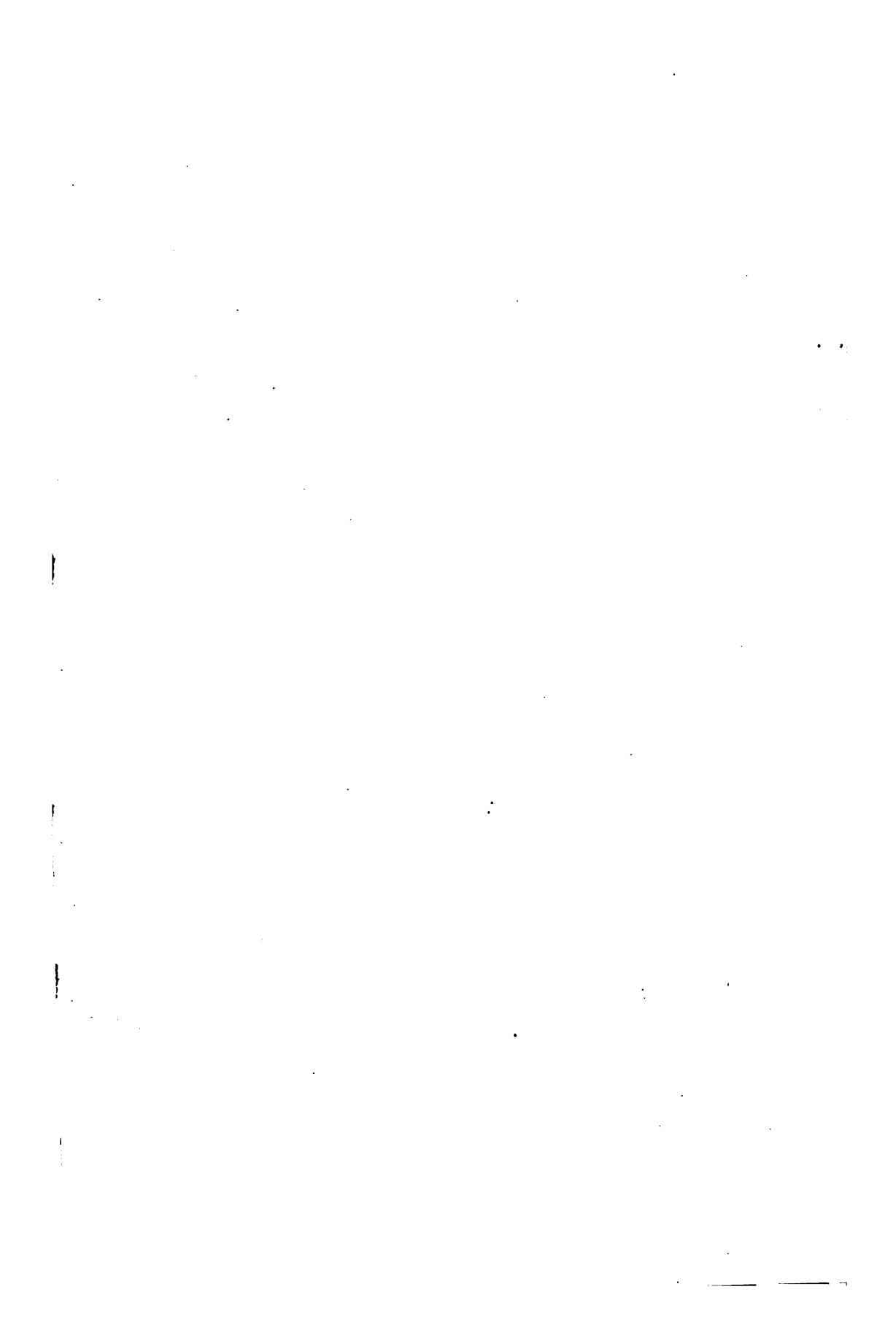
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A COURSE OF INSTRUCTION  
AND  
SYSTEM OF PROCEDURE  
IN  
QUALITATIV  
CHEMICAL ANALYSIS

BY  
ARTHUR A. NOYES

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PRELIMINARY EDITION PRINTED FOR THE  
USE OF THE CLASSES OF THE MASS-  
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# PART I.

## THE COURSE OF INSTRUCTION.

### LABORATORY EXPERIMENTS.

#### DETECTION OF THE BASIC CONSTITUENTS.

**Experiment 1.**—*Separation of the Basic Constituents into Groups.*—In connection with this experiment refer to Table II (page 34). Measure out with the aid of a 10 cc. graduate 5 cc. portions of the test-solutions of  $\text{AgNO}_3$ ,  $\text{Cu(NO}_3)_2$ ,  $\text{Al(NO}_3)_3$ ,  $\text{Zn(NO}_3)_2$ ,  $\text{Ca(NO}_3)_2$ , and  $\text{KNO}_3$ . Mix the portions in a conical flask, add 5 cc.  $\text{HNO}_3$  and 10 cc.  $\text{NH}_4\text{Cl}$  solution, and filter. Dilute the filtrate with water to a volume of 100 cc. Place it in a 200 cc. conical flask; insert a two-hole rubber stopper through which passes a tube leading to the bottom; and pass in a slow current of  $\text{H}_2\text{S}$ , until, upon shutting off the gas and shaking thoroly, the liquid smells strongly of it. Filter. Boil the filtrate till the  $\text{H}_2\text{S}$  is expelled, add to it 10 cc.  $\text{NH}_4\text{OH}$ , and note the result. Then add 3-5 cc.  $(\text{NH}_4)_2\text{S}$ . Shake the mixture and filter. Evaporate the filtrate to a volume of about 10 cc., filter, and to the cold solution add 30 cc.  $(\text{NH}_4)_2\text{CO}_3$  reagent and 30 cc. alcohol, shake, and filter. Evaporate the filtrate to dryness in a small casserole, and ignite the residue by moving the disk to and fro in a gas flame till no more white fumes come off.

In this experiment and all subsequent ones observe carefully everything that happens, and record it clearly and neatly in the note-book, together with the equations expressing all the chemical changes that take place. Before beginning the next experiment, write out on punched sheets of standard size answers to the "Questions" on the completed experiment printed at the end of the "Laboratory Experiments," and hand in the answers to the instructor.

*Notes.*—1. The solutions of constituents to be tested for, here called the test-solutions, are all so made up as to contain 10 mg. (10 milligrams) of the constituent per cubic centimeter of solution. The mixture used in this experiment will, therefore, contain 50 mg. of each of the elements silver, copper, aluminum, zinc, calcium, and potassium. The student should acquire the habit of working with definite quantities of the constituents and of noting the size of the precipitates which they yield. For a good qualitative analysis should not only show the presence or absence of the various constituents, but should also furnish an estimate of the proportions in which they are present.

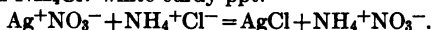


Test-solutions should not be used in place of reagents, nor reagents in place of test-solutions, since the concentrations are as a rule quite different. In regard to the concentrations of reagents, see Note 3, page 35, and Note 1, page 36.

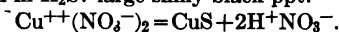
2. In the note-book the operations should be indicated very briefly; but everything that happens should be recorded fully, tho concisely. Thus the report of the first experiment may be made in the following form:

**Expt. 1.**—Added  $\text{HNO}_3$ : no change observed.

Added  $\text{NH}_4\text{Cl}$ : white curdy ppt.



Passed in  $\text{H}_2\text{S}$ : large slimy black ppt.



. . . . .

Solid substances involved in chemical reactions should be indicated by underlining their formulas. Largely ionized dissolved substances should be written with + and — signs attached to the formulas in such a way as to show the ions into which they dissociate. Slightly ionized dissolved substances should be distinguished by not attaching these signs to the formulas.

**Experiment 2.**—*Analysis of the Silver-Group.*—Mix a 20 cc. portion of the test-solution of  $\text{Pb}(\text{NO}_3)_2$  with 5 cc. portions of the test-solutions of  $\text{AgNO}_3$  and  $\text{Hg}_2(\text{NO}_3)_2$ , and treat the mixture by P. 11–15 (*i.e.*, by Procedures 11–15 of the System of Analysis described in Part II. See pages 35–36). Study Table III (page 35) before carrying out this experiment. At the time that the operations described in it are being executed read the Notes on P. 11–15.

**Experiment 3.**—*Precipitation by Hydrogen Sulfide.* To 10 cc. of the test-solution of  $\text{Hg}(\text{NO}_3)_2$  add 5 cc.  $\text{HNO}_3$ , 10 cc.  $\text{NH}_4\text{Cl}$  solution, and 75 cc. water. Treat this solution by the first paragraph of P. 21. In passing the  $\text{H}_2\text{S}$  in this experiment shut off the gas after only a few bubbles have passed through, shake the mixture, and note the color of the precipitate. Then pass in more  $\text{H}_2\text{S}$  till the solution becomes saturated. Keep the precipitate in a moist condition for use in Expt. 6.—Read Notes 1, 3, and 4, P. 21.

To 10 cc. of the test-solution of  $\text{H}_3\text{AsO}_4$  add 5 cc.  $\text{HNO}_3$ , 10 cc.  $\text{NH}_4\text{Cl}$  solution, and 75 cc. water. Treat this solution by P. 21.—Read Notes 2 and 5, P. 21.

**Experiment 4.**—*Effect of Acid on the Precipitation by Hydrogen Sulfide.*—Introduce into each of three test-tubes by means of a dropper 2 drops of the test-solution of  $\text{Cd}(\text{NO}_3)_2$ . Add to the first tube 1 cc.  $\text{HCl}$ , to the second 3 cc.  $\text{HCl}$ , and to the third 9 cc.  $\text{HCl}$ . Then add to each solution enough water to make the volume about 20 cc., and pass a slow current of  $\text{H}_2\text{S}$  into it for about a minute.—Repeat the last test (with 9 cc.  $\text{HCl}$ ), substituting  $\text{Cu}(\text{NO}_3)_2$  for the  $\text{Cd}(\text{NO}_3)_2$ .—Read Note 6, P. 21.

**Experiment 5.**—*Effect of Oxidizing Substances on Hydrogen Sulfide.*—To 50 cc. of the test-solution of  $\text{Fe}(\text{NO}_3)_3$  add 10 cc.  $\text{NH}_4\text{Cl}$  solution, 5 cc.  $\text{HNO}_3$ , and 35 cc. water, and pass in  $\text{H}_2\text{S}$  till the solution is saturated. Boil the solution (to coagulate the precipitate), filter, and add 10 cc. of the test-solution of  $\text{Ba}(\text{NO}_3)_2$ .—Read Notes 7 and 8, P. 21.

**Experiment 6.**—*Analysis of the Copper-Group: Behavior of Mercury.*—Treat the precipitate of  $\text{HgS}$  obtained in Expt. 3 by P. 23 and 24.—Read Notes 1–5, P. 23, and Notes 1–2, P. 24.

**Experiment 7.**—*Analysis of the Copper-Group: Behavior of Lead and Copper.*—Mix 10 cc. portions of the test-solutions of  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Cu}(\text{NO}_3)_2$ , add 5 cc.  $\text{HNO}_3$ , and 75 cc. water, and treat the mixture by P. 21, 23, 25, 26, 27, 29, and 30.—Refer to Table IV (page 42), and read Note 1, P. 25; the Notes on P. 26, 27, and 29; and Notes 1–2, P. 20.

**Experiment 8.**—*Analysis of the Copper-Group: Behavior of Bismuth and Cadmium.*—Mix together 10 cc. portions of the test-solutions of  $\text{Bi}(\text{NO}_3)_3$  and  $\text{Cd}(\text{NO}_3)_2$ . Add 5 cc.  $\text{HNO}_3$ , 10 cc.  $\text{NH}_4\text{Cl}$  solution, and 65 cc. water; and treat the mixture by P. 21 and P. 23–30.—Refer to Table IV, and read Note 2, P. 25 and the Notes on P. 28 and 30.

**Experiment 9.**—*Analysis of an Unknown Solution for Elements of the Copper-Group.*—Ask the instructor for an unknown solution containing elements of the copper-group (“unknown A”), and analyze 10 cc. of it by P. 21 and P. 23–30, first adding 5 cc.  $\text{HNO}_3$ .

*Note.*—Record the results of the analyses of unknown solutions in the same way as those of other experiments, except that the chemical equations need not be written. Sum up at the end, in the case of such analyses, the elements that are found to be present, giving also a rough estimate of the quantity of each per 10 cc. of solution. (Quantities less than 5 mg. may be reported as “small;” those from 5 to 50 mg., as “medium;” and those greater than 50 mg., as “large.”)

Keep all final tests in properly labelled test-tubes or flasks until the analysis has been completed and has been approved by the instructor.

**Experiment 10.**—*Separation of the Copper and Tin Groups.*—To a mixture of 10 cc. portions of the test-solutions of  $\text{Bi}(\text{NO}_3)_3$  and of  $\text{SbCl}_3$  add 5 cc.  $\text{HNO}_3$  and 75 cc. water, and treat the mixture by P. 21, 22 and 41. In P. 22 use ammonium monosulfide and only one 10 cc. portion of it; and in P. 41 omit the filtration and washing of the precipitate.—Refer to Table II (page 34); and read Note 1, P. 22 and Note 2, P. 41.

**Experiment 11.**—*Behaviors of Ammonium Monosulfide and Polysulfide on Acidification.*—Treat 5 cc. of ammonium monosulfide by P. 41 (omitting the filtration and washing of the precipitate).

Repeat the experiment with 5 cc. of ammonium polysulfide.

Repeat the experiment with a solution prepared by adding 1 cc. of the test-solution of  $\text{Cu}(\text{NO}_3)_2$  to 5 cc. of ammonium polysulfide, shaking, and filtering out the precipitate.

Read Notes 2-4, P. 22, and Notes 3-4, P. 41.

**Experiment 12.**—*Behavior of Ammonium Monosulfide and Ammonium Polysulfide towards Stannous Sulfide.*—Treat two 10 cc. portions of the test-solution of  $\text{SnCl}_2$  by P. 21, 22 and 41. In one case in P. 22 use 10 cc. of ammonium monosulfide, and in the other case use 10 cc. of ammonium polysulfide.—Read Notes 5-8, P. 22.

**Experiment 13.**—*Analysis of the Tin-Group.*—Mix together 10 cc. portions of the test-solutions of  $\text{AsCl}_3$ ,  $\text{SbCl}_3$ , and  $\text{SnCl}_4$ ; add 70 cc. water; and treat the mixture by P. 21. Filter with the aid of suction (see Note 1, P. 41), and suck the precipitate as dry as possible. Treat the precipitated sulfides by P. 42-47.—Refer to Table V (page 50), and read the Notes on P. 42-47.

**Experiment 14.**—*Analysis of an Unknown Solution for Elements of the Tin-Group.*—Ask for an unknown solution containing elements of the tin-group ("unknown B"), and analyze 10 cc. of it by P. 21 and P. 42-47.—In regard to recording the results, see the Note on Expt. 9.

**Experiment 15.**—*Analysis of an Unknown Solution for Elements of the Silver, Copper, and Tin Groups.*—Ask for an unknown solution containing elements of these groups ("unknown C"), and analyze 10 cc. of it by P. 11-47.

**Experiment 16.**—*Precipitation and Separation of the Aluminum and Iron Groups.*—Treat a mixture of 10 cc. portions of the test-solutions of  $\text{Al}(\text{NO}_3)_3$  and of  $\text{Fe}(\text{NO}_3)_3$  by P. 51-53.—Refer to Table II (page 34), and read Note 1, P. 51, and Notes 1-2, P. 52.

**Experiment 17.**—*Behavior of Elements of the Aluminum and Iron Groups towards Ammonium Hydroxide and Sulfide.*—To 5 cc. portions of the test-solutions of  $\text{Al}(\text{NO}_3)_3$ ,  $\text{Cr}(\text{NO}_3)_3$ ,  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{FeSO}_4$ ,  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{Mn}(\text{NO}_3)_2$ ,  $\text{Ni}(\text{NO}_3)_2$ , and  $\text{Co}(\text{NO}_3)_2$  in separate test-tubes add 5 or 6 drops of  $\text{NH}_4\text{OH}$ , and note the result. Then add 2-3 cc. more  $\text{NH}_4\text{OH}$ . Filter out the  $\text{Cr}(\text{OH})_3$  precipitate and heat the filtrate to boiling. To the other tubes in which there is still a precipitate add 5 cc.  $\text{NH}_4\text{Cl}$  solution. Finally add 1-2 cc.  $(\text{NH}_4)_2\text{S}$  to each tube. Filter out the  $\text{NiS}$  precipitate, and boil the filtrate. Record the results of all these tests in a single table, so as to show at a glance how each element behaves upon the addition of each reagent.—Read Notes 2-5 and 8-10, P. 51.

**Experiment 18.**—*Behavior of Elements of the Aluminum and Iron Groups towards Sodium Hydroxide and Peroxide.*—Repeat Expt. 17, substituting NaOH for  $\text{NH}_4\text{OH}$  and omitting the subsequent addition of  $\text{NH}_4\text{Cl}$  and  $(\text{NH}_4)_2\text{S}$ . To each of the mixtures to which NaOH has been added add gradually 0.4–0.5 g. solid  $\text{Na}_2\text{O}_2$ . Record the results in a single table as in Expt. 17.—Read Notes 3–7, P. 52.

*Note.*—Instead of weighing out solid substances, it is more convenient and usually sufficiently accurate to measure them in little horn-spoons which, when heaping full, hold 0.4–0.5 g. of the finely powdered solid compounds of sodium, potassium, and calcium that are used as reagents or as test substances in these experiments.

**Experiment 19.**—*Precipitation of Alkaline-Earth Elements by Ammonium Hydroxide in the Presence of Phosphate.*—Dissolve about 0.3 g.  $\text{Ca}_3(\text{PO}_4)_2$  in 5 cc.  $\text{HNO}_3$  and 10 cc. water. To one-half of the solution add  $\text{NH}_4\text{OH}$  till the mixture after shaking smells of it; filter out the precipitate; and add  $(\text{NH}_4)_2\text{CO}_3$  to the filtrate. To the other half add 10 cc. of the test-solution of  $\text{Fe}(\text{NO}_3)_3$ ; then add  $\text{NH}_4\text{OH}$ , filter, and add  $(\text{NH}_4)_2\text{CO}_3$ , as before.—Read Notes 6–7, P. 51.

**Experiment 20.**—*Behavior of Alkaline-Earth Phosphates in the Separation of the Aluminum-Group from the Iron-Group.*—Treat 10 cc. of the test-solution of  $\text{Ca}_3(\text{PO}_4)_2$  in  $\text{HNO}_3$  by the second paragraph of P. 52. Acidify the filtrate with  $\text{HNO}_3$ ; and test one-half of it for calcium by adding  $(\text{NH}_4)_2\text{CO}_3$ , and the other half for phosphate by adding  $(\text{NH}_4)_2\text{MoO}_4$  and warming.—Read Notes 8–9, P. 52.

**Experiment 21.**—*Analysis of the Aluminum-Group.*—Treat a mixture of 10 cc. of the test-solutions of  $\text{Al}(\text{NO}_3)_3$ ,  $\text{Cr}(\text{NO}_3)_3$ , and  $\text{Zn}(\text{NO}_3)_2$  by the second paragraph of P. 52 and by P. 53–57.—Refer to Table VI (page 60), and read the Notes on P. 53–57.

**Experiment 22.**—*Analysis of the Iron-Group: Behavior of Manganese and Iron.*—Treat a mixture of 10 cc. portions of the test-solutions of  $\text{Mn}(\text{NO}_3)_2$ ,  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{Co}(\text{NO}_3)_2$ , and  $\text{Ni}(\text{NO}_3)_2$  by the second paragraph of P. 52; and treat the precipitate thereby obtained by P. 61, 62, and 64. Reserve the ammoniacal filtrate obtained in P. 64 for use in Expt. 23.—Refer to the first part of Table VII (page 64), and read the Notes on P. 61, 62 and 64.

**Experiment 23.**—*Analysis of the Iron-Group: Behavior of Zinc, Nickel, and Cobalt.*—Treat the ammoniacal filtrate obtained in Expt. 22 by P. 66–70.—Refer to the last part of Table VII, and read the Notes on P. 66–70.

**Experiment 24.**—*Modification of the Analysis of the Iron-Group in the Presence of Phosphate for the Purpose of Detecting Alkaline-Earth Elements.*—Mix together 10 cc. portions of the test-solutions of  $\text{Fe}(\text{NO}_3)_3$ , of  $\text{Co}(\text{NO}_3)_2$ , and of  $\text{Ca}_3(\text{PO}_4)_2$  in  $\text{HNO}_3$ . Treat one tenth of this solution by P. 63, and treat the remainder of it by P. 65 and 66. To the filtrate obtained in P. 66 add 2–3 cc.  $(\text{NH}_4)_2\text{CO}_3$  reagent. —Read the Notes on P. 65.

**Experiment 25.**—*Analysis of Unknown Solutions for Elements of the Aluminum and Iron Groups.*—Ask the instructor for two unknown solutions for this purpose (“unknowns D and E”), and treat 10 cc. of each solution by P. 51–70.

**Experiment 26.**—*Determination of the State of Oxidation in which Iron is Present.*—To separate 5 cc. portions of the test-solution of  $\text{Fe}(\text{NO}_3)_3$  add 1–2 cc. of solutions of  $\text{KSCN}$ , of  $\text{K}_4\text{Fe}(\text{CN})_6$ , and of  $\text{K}_3\text{Fe}(\text{CN})_6$ .

To 15 cc. of the test-solution of  $\text{FeSO}_4$  in a test-tube add 1–2 cc. of  $\text{H}_2\text{SO}_4$  and 0.5 g. iron filings, in order to reduce any ferric salt that may be present. After 5–10 minutes decant the solution from the iron, and add to separate 3–4 cc. portions of it 1–2 cc. of solutions of  $\text{KSCN}$ ,  $\text{K}_4\text{Fe}(\text{CN})_6$ , and  $\text{K}_3\text{Fe}(\text{CN})_6$ .

**Experiment 27.**—*Precipitation of the Alkaline-Earth Group.*—To 1 cc. of the test-solution of  $\text{Mg}(\text{NO}_3)_2$  add 10 cc. water and 1–2 cc.  $(\text{NH}_4)_2\text{CO}_3$  reagent and shake the mixture for 2–3 minutes. Then add (in accordance with P. 81) 30 cc.  $(\text{NH}_4)_2\text{CO}_3$  reagent and 30 cc. 95 per cent alcohol, and shake for 2–3 minutes more.

To 1 cc. of the test-solution of  $\text{Ca}(\text{NO}_3)_2$  add 10 cc. water and 1–2 cc.  $(\text{NH}_4)_2\text{CO}_3$  reagent, shake, and after 2–3 minutes filter out the precipitate. To the filtrate add 30 cc.  $(\text{NH}_4)_2\text{CO}_3$  reagent and 30 cc. 95 per cent alcohol.—Read the Notes on P. 81.

**Experiment 28.**—*Analysis of the Alkaline-Earth Group.*—Mix together in a small flask 5 cc. portions of the test-solutions of  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{NO}_3)_2$ , and  $\text{Mg}(\text{NO}_3)_2$ . Add to the mixture 30 cc.  $(\text{NH}_4)_2\text{CO}_3$  reagent and 30 cc. 95 per cent alcohol, and shake it for about 5 minutes. (In an actual analysis, in order to insure the complete precipitation of magnesium, it is necessary to wait at least half an hour before filtering, as directed in P. 81.) Filter out the precipitate and treat it by P. 82–88.—Refer to Table VIII (page 71), and read the Notes on P. 82–88.

**Experiment 29.**—*Analysis of an Unknown Solution for Elements of the Alkaline-Earth Group.*—Ask the instructor for an unknown solution for this purpose (“unknown F”), and analyze 10 cc. of it by P. 81–88.

**Experiment 30.**—*Analysis of the Alkali-Group.*—Mix together 10 cc. portions of the test-solutions of  $\text{KNO}_3$  and  $\text{NaNO}_3$ , add to the mixture 10 cc.  $\text{NH}_4\text{Cl}$  solution and 10 cc.  $(\text{NH}_4)_2\text{CO}_3$  reagent, and treat it by P. 91–93.—Refer to Table IX (page 76), and read the Notes on P. 91–93.

**Experiment 31.**—*Analysis of Unknown Solutions for All the Basic Constituents.*—Ask the instructor for two unknown solutions for this purpose (“unknowns G and H”), and analyze 10 cc. of each of them by P. 11–93.

*Note.*—In complete analyses of this kind where a number of different precipitates and filtrates are successively obtained, any of these that are set aside, even temporarily, should be distinctly labelled, in order to avoid mistakes. A convenient method of doing this is to mark on the label simply the Procedure by which the precipitate or filtrate is next to be treated; thus the  $\text{H}_2\text{S}$  precipitate would be marked P. 22, and the filtrate from it P. 51. The final tests for any element may be marked Test for Pb, Test for Al, etc.

#### DETECTION OF THE ACIDIC CONSTITUENTS.

**Experiment 32.**—*Distillation with Phosphoric Acid and Detection of Sulfate.*—Mix 3 cc. portions of the test-solutions of  $\text{NaCO}_3$ ,  $\text{Na}_2\text{SO}_3$ , and  $\text{K}_2\text{SO}_4$ , and treat this mixture (in place of the “2 g. of the finely powdered substance”) by P. 101. Cork the flask containing the first distillate (after acidifying it with  $\text{HAc}$ ), and keep it for use in Expt. 33. Add to the second distillate  $\text{AgNO}_3$  solution. Treat the third distillate by P. 112.—Refer to Table X (page 79), and read the Notes on P. 101 and 112.

**Experiment 33.**—*Detection of Carbonate and Sulfite or Thiosulfate.*—Treat the whole of the first distillate obtained in Expt. 32 by the first paragraph of P. 102.—In the case of each one of Expts. 33–36 refer to the part of Table XI (page 82) that relates to that experiment, and read the Notes on the Procedure involved in it.

**Experiment 34.**—*Detection of Iodin-Liberating Constituents.*—Treat 10 cc. of the test-solution of  $\text{NaOCl}$  (which contains also an equivalent quantity of  $\text{NaCl}$ ) by the first paragraph of P. 101. Treat the whole distillate so obtained by the first, second and fourth paragraphs of P. 103. Test the aqueous layer finally obtained by adding to it 2–3 cc.  $\text{HNO}_3$  and 2–3 cc.  $\text{AgNO}_3$  solution (instead of by P. 110).

Treat 3 cc. of the test-solution of  $\text{KNO}_2$  by the first two paragraphs of P. 103.

**Experiment 35.**—*Confirmatory Test for Nitrite.*—Treat 1 cc. of the test-solution of  $\text{KNO}_2$  by P. 104.

**Experiment 36.**—*Detection of Sulfide.*—To 3 cc. of the test-solution of  $\text{Na}_2\text{S}$  add 3 cc.  $\text{HAc}$  and 2–3 cc.  $\text{Cd}(\text{NO}_3)_2$  solution.

**Experiment 37.**—*Detection of Cyanide.*—Treat 3 cc. of the test-solution of  $\text{KCN}$  by P. 106.—Refer to Table XI, and read Notes 1–3, P. 106.

**Experiment 38.**—*Analysis of an Unknown Solution for Acidic Constituents Passing into the First Distillate.*—Ask the instructor for an unknown solution for this purpose ("unknown I"), and treat 10 cc. of it by the first paragraph of P. 101. Treat the distillate thereby obtained by P. 102–106.

**Experiment 39.**—*Constituents Precipitable by Silver Nitrate.*—Treat in separate test-tubes 3 cc. of the test-solutions of  $\text{KCN}$ ,  $\text{KI}$ , and  $\text{Na}_2\text{S}$  by the first paragraph of P. 107.—Read the Notes on P. 107.

**Experiment 40.**—*Detection of Thiocyanate.*—To 3 cc. of the test-solution of  $\text{KSCN}$  add 2–3 drops of  $\text{FeCl}_3$  solution and 2–3 drops  $\text{HCl}$ .—Read the Notes on P. 108.

**Experiment 41.**—*Detection of Free Halogen and of the Halides.*—Mix together 3 cc. portions of the test-solutions of  $\text{KCl}$ ,  $\text{KBr}$ ,  $\text{KI}$ , and  $\text{I}_2$ . Treat the mixture by P. 109 and 110, omitting the treatment of the chloroform-extract referred to in the last paragraph of P. 109.—Refer to the middle part of Table XII (page 88), and read the Notes on P. 109 and 110.

**Experiment 42.**—*Detection of Nitrate.*—Treat 3 cc. of the test-solution of  $\text{KNO}_3$  by P. 111.—Read the Notes on P. 111.

**Experiment 43.**—*Analysis of an Unknown Solution for Acidic Constituents Passing into the Second and Third Distillates.*—Ask the instructor for an unknown solution for this purpose ("unknown J"), and treat 10 cc. of it by P. 101. Treat the second and third distillates by P. 107–112.—Refer to Table XII (page 88).

**Experiment 44.**—*Detection of Borate.*—Treat 0.2–0.3 g. of solid borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) by P. 113.—In connection with each one of Expts. 44–49 refer to Table XIII (page 93), and read the Notes on the Procedure involved in the experiment.

**Experiment 45.**—*Detection of Fluoride.*—Treat 0.2–0.3 g. of solid  $\text{CaF}_2$  by P. 114.



**Experiment 46.**—*Detection of Phosphate.*—Treat 0.2–0.3 g. of solid  $\text{Ca}_3(\text{PO}_4)_2$  by P. 115.

**Experiment 47.**—*Detection of Hypochlorite.*—Treat 3 cc. of the test-solution of  $\text{NaOCl}$  by P. 116.

**Experiment 48.**—*Detection of Chlorate.*—Mix together 3 cc. portions of the test-solutions of  $\text{KCl}$  and  $\text{KClO}_3$ , add 50 cc. water and 10 cc.  $\text{HNO}_3$ , and treat the mixture by the last half of P. 117, beginning at “Add  $\text{AgNO}_3$ . . . .”

**Experiment 49.**—*Detection of Sulfite and Thiosulfate.*—Mix together 3 cc. portions of the test-solutions of  $\text{Na}_2\text{SO}_3$  and  $\text{Na}_2\text{S}_2\text{O}_3$ , and treat the mixture (instead of “0.5 g. of the finely powdered original substance”) by P. 118.

PREPARATION OF THE SOLUTION AND COMPLETE ANALYSES IN THE  
CASE OF UNKNOWN SOLID SUBSTANCES.

**Experiment 50.**—*Substances Soluble in Water or Dilute Acid.*—Ask the instructor for two such unknown substances (“unknowns 1 and 2”), and treat portions of each of them by P. 1, by P. 2 followed by P. 11–93, and by P. 101–118.—Read the Notes on P. 1 and 2.—Record and report the results in the note-book as directed in the Notes on Expts. 9 and 31. In the case of a solid substance report not only the constituents and the proportions of them present, but state the compound or compounds of which the substance seems to be mainly composed.

*Note.*—In analyzing unknown solids the quantity taken for the analysis should be weighed (within 0.1 g.) on a rough balance, not guessed at nor estimated in the way suggested in the Note to Expt. 18.

**Experiment 51.**—*Non-Metallic Substances Requiring Treatment with Concentrated Acids.*—Ask the instructor for three such substances (“unknowns 3, 4, and 5”), and treat portions of each of them by P. 1, by P. 2–3 (or 2–4, if necessary,) followed by P. 11–93 (or 21–93), and by P. 101–118. If there is any undissolved residue (of silica or silicate) at the end of P. 4, disregard it in these analyses.—Refer to Table I (page 23), and read Notes 1–4, P. 3, and Notes 1–2, P. 4.

**Experiment 52.**—*Alloys Dissolved by Concentrated Acids.*—Ask the instructor for two such alloys (“unknowns 6 and 7”), and treat 0.5 g. of each by P. 3–4 and P. 11–70 (or P. 21–70).—Read Notes 5–9, P. 3, and Note 3, P. 4.

**Experiment 53.**—*Mineral Substances or Metallurgical Products Not Completely Dissolved by Concentrated Nitric and Hydrochloric Acids.*—Ask the instructor for such a substance ("unknown 8"). Treat 1 g. of it by P. 2-4. Treat the solution obtained in P. 4 by P. 21-93, and the residue obtained in P. 4 by P. 7, followed by P. 21-88. Reserve, however, one half of the aqueous extract of the fused mass obtained in P. 7, and test it for acidic constituents as described in the last four paragraphs of P. 119.—Read the Notes on P. 7 and P. 119. Treat another 1 g. portion of the substance by P. 101, and test the distillates for carbonate, sulfide, chloride, and sulfate.

Ask the instructor for two more such substances ("unknowns 9 and 10"). Treat 1 g. of each of them by P. 2-6, followed by P. 11-93.—Refer to Table I (page 23), and read the Notes on P. 5 and 16.—Treat another 1 g. portion of each of the substances by P. 101, and test the distillates for carbonate, sulfide, chloride, and sulfate. Treat a third 1 g. portion of each of them by P. 119.

**Experiment 54.**—*Substances Containing Organic Matter.*—Ask the instructor for such a substance ("unknown 11"), and treat portions of it by P. 1, by P. 8 followed by P. 11-93, and by P. 101 followed by P. 102-118.—Read the Notes on P. 8.

## QUESTIONS ON THE EXPERIMENTS.

**Experiment 1.**—1. In precipitating the silver-group in an actual analysis could the  $\text{NH}_4\text{Cl}$  be replaced by  $\text{NaCl}$ ? by  $\text{HCl}$ ? (*In the case of all questions which can be answered by "yes" or "no," give the reasons for the answer.*)

2. If the  $\text{NH}_4\text{Cl}$  were not added, what would happen to the silver in the subsequent parts of the experiment? (When the answer to a question is not known and it can be learned by a simple experiment, the student should try the experiment.)

3. Of the six basic constituents present in the mixture why is silver the only one that is precipitated by  $\text{NH}_4\text{Cl}$ ?

4. If enough  $\text{H}_2\text{S}$  were not used to precipitate all the copper, how would it behave in the subsequent parts of the experiment?

5. What is the first reaction that takes place when  $\text{NH}_4\text{OH}$  is added to the filtrate from the  $\text{H}_2\text{S}$  precipitate?

6. If the  $\text{H}_2\text{S}$  had not been expelled from the solution before adding the  $\text{NH}_4\text{OH}$ , would there be any difference in the precipitate produced by the  $\text{NH}_4\text{OH}$ ?

7. What would happen to the  $(\text{NH}_4)_2\text{S}$  if it were added directly to the filtrate from the  $\text{H}_2\text{S}$  precipitate, without first adding  $\text{NH}_4\text{OH}$ ?

8. What happens to the  $(\text{NH}_4)_2\text{S}$  when the filtrate from the  $(\text{NH}_4)_2\text{S}$  precipitate is evaporated?

9. If all the basic constituents had been present in the original mixture used for this experiment, what ones would have been precipitated by (a)  $\text{NH}_4\text{Cl}$ , (b)  $\text{H}_2\text{S}$ , (c)  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{S}$ , (d)  $(\text{NH}_4)_2\text{CO}_3$ ? (e) What ones would have been left with the potassium in the filtrate from the  $(\text{NH}_4)_2\text{CO}_3$  precipitate?

**Experiment 2.\***—1. What would be meant by "equivalent quantities of lead nitrate and ammonium chloride?"

2. What is meant by the expression "one equivalent of salt" used in Note 3, P. 11?

3. In making up a 1-normal solution of  $\text{NH}_4\text{Cl}$ , how many grams of the salt should be weighed out and how much water should be added to it?

4. How much normal are the test-solutions of  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{AgNO}_3$ , and  $\text{Hg}_2(\text{NO}_3)_2$  used in this experiment? (See Note 1, Expt. 1.)

5. How many cubic centimeters of the  $\text{NH}_4\text{Cl}$  solution would be required to furnish a quantity of chloride equivalent to the quantity of lead, silver, and mercury present in the mixture used in this experiment?

6. Why is so large an excess of  $\text{NH}_4\text{Cl}$  added? (The word *excess* signifies the quantity added beyond the equivalent quantity theoretically required to produce the reaction in question.)

7. The solubility of  $\text{PbCl}_2$  at  $20^\circ$  in water is 9.8 g. per liter and in a 0.2-normal  $\text{NH}_4\text{Cl}$  is 2.6 g. per liter. Explain why the  $\text{NH}_4\text{Cl}$  diminishes the solubility.

8. From the preceding data calculate how many milligrams of lead would have to be present in 40 cc. water at  $20^\circ$ , in order that any precipitation of  $\text{PbCl}_2$  may result on adding to it 10 cc.  $\text{NH}_4\text{Cl}$  solution.

9. Look up in Seidell's "Solubilities" the solubility of  $\text{PbCl}_2$  in boiling water; and calculate how much boiling water would be required to dissolve 500 mg.  $\text{PbCl}_2$ .

10. Look up in Seidell's "Solubilities" the solubility of  $\text{AgCl}$  at  $100^\circ$ , and calculate how many milligrams of silver might be lost if the chloride precipitate were washed with 100 cc. boiling water.

\* The atomic weights needed in answering some of the following questions are: O, 16.00; H, 1.008; N, 14.01; Cl, 35.46; Pb, 207.1; Ag, 107.9; Hg, 200.6.

11. In testing for lead in P. 13, explain why the addition of  $\text{H}_2\text{SO}_4$  to the solution and to the wash-water diminishes the solubility of the precipitate, and thus increases the delicacy of the test.

12. Look up the solubility of  $\text{PbSO}_4$  in water at  $20^\circ$ , and find the ratio of the minimum amounts of lead that could be precipitated from a  $\text{Pb}(\text{NO}_3)_2$  solution by adding to it amounts of  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$  equivalent to the lead present.

13. What other elements besides lead might be precipitated by adding  $\text{H}_2\text{SO}_4$  to a solution in which they were present?

14. Since these other elements are precipitable by  $\text{H}_2\text{SO}_4$ , why does the formation of a precipitate in P. 13 show the presence of lead?

15. Would the validity of the conclusion that it is present be effected if the group-precipitate produced by  $\text{HCl}$  was not washed?

16. Explain by the solubility-product principle why the fact that  $\text{PbAc}_2$  is a slightly ionized substance should cause  $\text{PbSO}_4$  to dissolve much more readily in  $\text{NH}_4\text{Ac}$  solution than in water.

17. Would you expect  $\text{PbCrO}_4$  also to be more soluble in  $\text{NH}_4\text{Ac}$  solution than in water? Why or why not? If so, why does  $\text{PbCrO}_4$  precipitate from the same  $\text{NH}_4\text{Ac}$  solution that dissolves  $\text{PbSO}_4$ ?

18. Arrange all the compounds of lead thus far met with in the order in which their solubility in water decreases.

19. Explain by the solubility-product principle why the formation of the complex salt  $\text{Ag}(\text{NH}_3)_2^+\text{Cl}^-$  causes  $\text{AgCl}$  to be much more soluble in  $\text{NH}_4\text{OH}$  solution than in water.

20. Formulate the mass-action expression for the equilibrium between the complex cation  $\text{Ag}(\text{NH}_3)_2^+$  and its constituents. Show by reference to this expression and the solubility-product principle why the addition of  $\text{HNO}_3$  causes  $\text{AgCl}$  to be precipitated out of its solution in  $\text{NH}_4\text{OH}$ .

**Experiments 3 and 4.\***—1. In precipitating with  $\text{H}_2\text{S}$  in P. 21 what is the reason for adding 5 cc.  $\text{HNO}_3$  and diluting the solution to 100 cc.? Why not use less acid and thus avoid all risk of failing to precipitate the elements of the copper and tin groups?

2. In passing in  $\text{H}_2\text{S}$ , at what stage in the process does the solution after shaking begin to smell of the gas?

3. Why would the minimum quantity of an element that would just give a precipitate be larger if in P. 21 the solution were treated with  $\text{H}_2\text{S}$  in an open beaker, instead of in the closed flask?

4. Give two reasons why the minimum quantity of an element that would just give a precipitate would be larger if the solution were saturated with  $\text{H}_2\text{S}$  at  $80^\circ$ , instead of at  $20^\circ$ .

5. Assuming that the solubility (in formula-weights per liter) of  $\text{CdS}$  in water is ten times as great as that of  $\text{CuS}$ , calculate by the principles discussed in Note 6, P. 21, the ratio of the hydrogen-ion concentrations at which the precipitation of the copper and cadmium will barely take place when the concentration of each of them has any definite value (for example, 0.0001 formula-weights per liter).

6. By what reaction is the  $\text{HNO}_3$  "destroyed" when the arsenic solution to which  $\text{HCl}$  has been added is evaporated to dryness? Could  $\text{HCl}$  be destroyed in the same way by evaporating a solution of chloride with  $\text{HNO}_3$ ?

7. If the  $\text{HNO}_3$  were not so destroyed, what reaction would take place between it and the  $\text{H}_2\text{S}$  when the latter is passed into the hot, strongly acid solution? Write the equation expressing it.

\*Questions on two or more experiments should be answered after the last of the experiments is completed.

**Experiment 5.**—1. What substances besides ferric salts might be present which would cause precipitation of sulfur in P. 21?

2. What is the bearing on the scheme of analysis of the fact illustrated by the last part of this experiment?

**Experiment 6.**—1. Describe in detail an experiment by which one could determine whether HgS dissolves to an appreciable extent when treated with hot dilute  $\text{HNO}_3$  in the way directed in P. 23.

2. Explain by the solubility-product principle the fact that CuS, which is only slightly soluble in hot dilute HCl, dissolves readily in hot dilute  $\text{HNO}_3$  of the same concentration.

3. Explain the fact that HgS, unlike CuS, does not dissolve even in hot dilute  $\text{HNO}_3$ .

4. Why is a black residue left undissolved by  $\text{HNO}_3$  not sufficient evidence of the presence of mercury?

5. Suggest a reason why in the confirmatory test for mercury the addition of HCl with the  $\text{SnCl}_2$  tends to prevent the immediate reduction of the  $\text{Hg}_2\text{Cl}_2$  to Hg.

**Experiment 7.**—1. Why does the evaporation with  $\text{H}_2\text{SO}_4$  convert the salts present into sulfates? Could sulfates be converted into nitrates by evaporating with a large excess of  $\text{HNO}_3$ ?

2. Explain with reference to the solubility-product principle why  $\text{PbSO}_4$  is much more soluble in dilute  $\text{HNO}_3$  than in water. ( $\text{H}_2\text{SO}_4$  in dilute solution is dissociated almost completely into  $\text{H}^+$  and  $\text{HSO}_4^-$ ; but the latter ion is only to a moderate extent dissociated into  $\text{H}^+$  and  $\text{SO}_4^{2-}$ ).

3. What effect, as compared with that of  $\text{HNO}_3$ , would HCl have on the solubility of  $\text{PbSO}_4$ ? What effect would  $\text{KNO}_3$  have? Give reasons. ( $\text{K}_2\text{SO}_4$  in dilute solution, like other univalent salts, but unlike  $\text{H}_2\text{SO}_4$ , is almost completely dissociated into the simple ions,  $\text{K}^+$  and  $\text{SO}_4^{2-}$ , with formation of only a small proportion of the intermediate ion,  $\text{KHSO}_4$ .)

4. Devise and describe an experiment which would determine whether PbS is more or less soluble in water than  $\text{PbSO}_4$ .

5. To what constituent is the deep blue color of the ammoniacal copper solution due?

6. Explain with the aid of the mass-action expressions involved why  $\text{Cu}(\text{OH})_2$ , a substance very slightly soluble in water, is not precipitated by the  $\text{NH}_4\text{OH}$ . Show that the presence of the  $(\text{NH}_4)_2\text{SO}_4$  in the solution must diminish the tendency of it to precipitate.

7. If the lead were not removed by the addition of  $\text{H}_2\text{SO}_4$ , would it be precipitated as  $\text{Pb}(\text{OH})_2$  on the addition of  $\text{NH}_4\text{OH}$ ? What knowledge in regard to lead compounds would enable one to predict whether or not this precipitation would take place?

8. If  $\text{K}_4\text{Fe}(\text{CN})_6$  be added in P. 29 to the ammoniacal solution (without neutralizing it with HAc), no precipitate is produced unless a fairly large quantity of copper is present. Explain this fact.

9. What external evidence is there that the complex copper-ammonia ion is completely decomposed when KCN is added to the solution?

10. Explain with the aid of the mass-action expressions involved why  $\text{Cu}_2\text{S}$ , a very slightly soluble sulfide, does not precipitate when  $\text{H}_2\text{S}$  is passed into the cyanide solution.

**Experiment 8.**—1. Explain by the mass-action law why the precipitation of  $\text{BiOCl}$  would be prevented by the presence of much  $\text{HCl}$ .

2. What would be the form of the solubility-product expression for a salt like  $\text{BiOCl}$ ?

3. Show with the aid of this expression that  $\text{HNO}_3$  should increase the solubility of  $\text{BiOCl}$ ; also that  $\text{HCl}$  should increase it, but not so much. Take into account the fact that water ionizes (to a very slight extent) into  $\text{H}^+$  and  $\text{O}^-$ .

4. How would the delicacy of the oxychloride test be affected if the bismuth solution were poured into a  $\text{NaCl}$  solution, instead of into water?

5. Lead hydroxide, like  $\text{Sn}(\text{OH})_2$ , is an amphoteric substance. What is meant by this statement? What experiments might be made to determine whether it is true?

6. Show from the solubility-product expressions that, if  $\text{Cd}_2\text{Fe}(\text{CN})_6$  is much more soluble than  $\text{Cu}_2\text{Fe}(\text{CN})_6$ , the former can not be precipitated till enough  $\text{K}_4\text{Fe}(\text{CN})_6$  has been added to precipitate practically all the copper.

7. As shown in Expt. 4,  $\text{CdS}$  is a much more soluble sulfide than  $\text{CuS}$ . Why is  $\text{CdS}$  precipitated by  $\text{H}_2\text{S}$  from the  $\text{KCN}$  solution, while  $\text{CuS}$  is not?

8. Silver forms a complex cyanide  $\text{K}^+\text{Ag}(\text{CN})_2^-$  analogous to  $\text{K}^+\text{Cu}(\text{CN})_2^-$ , and  $\text{Ag}_2\text{S}$  is not precipitated from its solution by  $\text{H}_2\text{S}$ . Zinc and nickel form complex cyanides,  $\text{K}_2^+\text{Zn}(\text{CN})_4^-$  and  $\text{K}_2^+\text{Ni}(\text{CN})_4^-$ , analogous to  $\text{K}_2\text{Cd}(\text{CN})_4$ , and  $\text{H}_2\text{S}$  produces a precipitate in their solutions. What general conclusion would seem to be justified by these facts as to the stability of complex cyanides?

9. Describe in the form of a Procedure which might be substituted for P. 30 another method of separating cadmium and copper based on the results of Expt. 4.

10. What experiments would it be best to try in order to determine whether the new procedure described in the answer to Question 9 works satisfactorily?

**Experiments 10–12.**—1. Write chemical equations expressing the two stages of the hydrolysis of  $(\text{NH}_4)_2\text{S}$ . Explain by the ionic theory and the mass-action law why this hydrolysis takes place, taking into account the fact that water is ionized to a slight extent into  $\text{H}^+$  and  $\text{OH}^-$ .

2. Why does not  $\text{Bi}_2\text{S}_3$  dissolve in  $(\text{NH}_4)_2\text{S}$ , just as  $\text{Sb}_2\text{S}_3$  does?

3. Why does not  $\text{SnS}$  dissolve in ammonium monosulfide as well as in ammonium polysulfide?

4. Make a table showing the solubility of each of the sulfides of the copper and tin groups in both ammonium monosulfide and ammonium polysulfide. Indicate in each case whether the sulfide is readily soluble, slightly soluble, or practically insoluble.

5. Why not use in all cases ammonium polysulfide, since this readily dissolves all the tin-group sulfides? Why is the precipitate first treated with a small quantity of it, even tho this makes necessary a second treatment?

6. What illustration does the separation of the copper-group from the tin-group by ammonium polysulfide afford of the fact that a substance may be readily soluble in a solvent and yet not be dissolved by it when an insoluble substance is present with it?

7. Why does the addition of  $\text{HCl}$  to a solution of  $(\text{NH}_4)_2\text{SnS}_3$  cause the precipitation of  $\text{SnS}_2$ ?

8. Why does not the tendency of copper to form the complex copper-ammonia ion cause  $\text{CuS}$  to dissolve in  $\text{NH}_4\text{OH}$ ?

**Experiment 13.**—1. In treating the sulfides with concentrated HCl why would much more of the  $\text{As}_2\text{S}_5$  dissolve if the solution were boiled than if it were heated to  $100^\circ$  without boiling?

2. Why does the addition of  $\text{KClO}_3$  cause the  $\text{As}_2\text{S}_5$  to dissolve even in the more dilute HCl?

3. What does the fact that  $\text{H}_3\text{AsO}_4$  does not combine with HCl forming  $\text{AsCl}_5$  show in regard to the ionization of  $\text{H}_3\text{AsO}_4$ ? Is it an amphoteric substance?

4. What is the expression for the solubility-product in the case of  $\text{MgNH}_4\text{AsO}_4$ ? Why does the hydrolysis of this salt increase its solubility? Why is that hydrolysis decreased by an excess of  $\text{NH}_4\text{OH}$ ? How is the hydrolysis affected by the presence of  $\text{NH}_4\text{Cl}$ ? Would  $\text{NH}_4\text{Cl}$  affect the solubility in any other way?

5. What is a saturated solution? a supersaturated one? By what treatments can a precipitate be made to separate from a supersaturated solution?

6. Why does  $\text{MgNH}_4\text{AsO}_4$  dissolve readily in HCl?

7. What difference in the ionization causes the behavior of arsenic acid towards  $\text{H}_2\text{S}$  to be so different from that of other elements of the copper and tin groups?

8. What determines whether one metal will be precipitated from its solution by another? Could one predict by this principle that zinc would precipitate antimony from the knowledge that zinc precipitates tin and tin precipitates antimony?

9. Explain why antimony precipitates on the platinum rather than on the tin.

10. How would the result be different if the tin did not touch the platinum?

11. Why does the tin dissolve in HCl more readily when it is in contact with the platinum?

12. In the confirmatory test for tin how does the precipitation of a mercury compound show the presence of tin?

**Experiment 16.**—1. In an actual analysis how many cubic centimeters of  $\text{NH}_4\text{OH}$  would be required to neutralize the 5 cc.  $\text{HNO}_3$  that are added before precipitating with  $\text{H}_2\text{S}$ ?

2. How much more  $\text{NH}_4\text{OH}$  would be needed to neutralize the solution if 500 mg. Cu had been present in the form of  $\text{Cu}(\text{NO}_3)_2$  in the solution precipitated by  $\text{H}_2\text{S}$ ?

3. How does testing the vapors above the solution with  $\text{PbAc}_2$ -paper show that an excess of  $(\text{NH}_4)_2\text{S}$ , a non-volatile salt, has been added?

4. Why is the  $(\text{NH}_4)_2\text{S}$  precipitate treated first with cold HCl? Why is  $\text{HNO}_3$  subsequently added?

**Experiments 17 and 18.**—1. Which elements are soluble, *a*, in excess of  $\text{NH}_4\text{OH}$  (in the presence of  $\text{NH}_4\text{Cl}$ ), but not in excess of NaOH; *b*, in excess of NaOH, but not of  $\text{NH}_4\text{OH}$  (in presence of  $\text{NH}_4\text{Cl}$ ); *c*, in excess both of  $\text{NH}_4\text{OH}$  and of NaOH; *d*, neither in excess of NaOH nor of  $\text{NH}_4\text{OH}$  (in presence of  $\text{NH}_4\text{Cl}$ )?

2. What are the explanations of the four typical cases *a*, *b*, *c*, *d*, referred to in the preceding question?

3. Could the hydroxide of an element which does not form a complex ammonia cation be soluble in  $\text{NH}_4\text{OH}$  and not in NaOH? Could an amphoteric hydroxide be readily soluble in NaOH and entirely insoluble in  $\text{NH}_4\text{OH}$ ?

4. Show by formulating and combining the two mass-action equations involved that the quantity of aluminum dissolved (as  $\text{AlO}_2^-$ ) in the presence of a base is proportional to the  $\text{OH}^-$  concentration in the solution.

5. If 0.09 at. wt. of aluminum is dissolved in a 0.1 normal NaOH solution saturated with  $\text{AlO}_3\text{H}_3$  in which the value of  $(\text{OH}^-)$  is 0.01 normal, how much aluminum would be dissolved in a solution 0.1 normal both in  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{Cl}$ , in which the value of  $(\text{OH}^-)$  is 0.00002 normal?



6. Name all the elements that form ammonia complexes in all the groups thus far considered. What can be said as to the position of these elements in the periodic system? (Refer to a text-book of Inorganic Chemistry.)

7. If in an actual analysis no precipitate is obtained on the addition of  $\text{NH}_4\text{OH}$ , what conclusion may be drawn?

8. Which of the hydroxides precipitated by  $\text{NaOH}$  undergo change on the addition of  $\text{Na}_2\text{O}_2$ , and into what compound is each of these hydroxides converted?

9. What substances are produced by the action of  $\text{Na}_2\text{O}_2$  on water?

**Experiments 19 and 20.**—1. What does Expt. 19 show in regard to the behavior of the alkaline-earth elements in an actual analysis?

2. What must be the explanation of the fact that the phosphate combines with the iron rather than the calcium when both these elements are present?

3. If phosphate is known to be present, is it necessary to test for alkaline-earth elements in the filtrate from the  $(\text{NH}_4)_2\text{S}$  precipitate?

4. If the original substance were soluble in water, would it be necessary to test for these elements in the  $(\text{NH}_4)_2\text{S}$  precipitate?

5. If  $\text{CaCO}_3$  were substituted for  $\text{Ca}_3(\text{PO}_4)_2$  in the first part of Expt. 19, would the result have been the same? Would it have been the same if the original substance in an actual analysis had been  $\text{CaCO}_3$  and the solution had been previously treated by P. 21?

**Experiment 21.**—1. Since  $\text{AlCl}_3$  is readily soluble in water, what precautions must be observed in order that the confirmatory test for aluminum may be delicate?

2. Give two or three reasons why the dropping of  $\text{H}_2\text{SO}_4$  into commercial  $\text{HCl}$  causes  $\text{HCl}$  gas to be evolved.

3. By what reagent other than  $\text{BaCl}_2$  could the chromate be precipitated? What disadvantage would there be in the use of this reagent?

4. How can sulfate be present in the solution to which  $\text{BaCl}_2$  is added?

5. If, without adding  $\text{BaCl}_2$ ,  $\text{H}_2\text{S}$  were passed into the  $\text{HAc}$  solution, what chemical change would the chromate undergo? Write the equation expressing it.

6. What happens to nitrates, such as  $\text{Zn}(\text{NO}_3)_2$  or  $\text{Co}(\text{NO}_3)_2$ , when they are ignited, as in the confirmatory test for zinc?

**Experiment 22.**—1. What are the oxides of manganese corresponding to its three stages of oxidation occurring in P. 61 and 62? What is the valence of manganese in each of these oxides? How do they differ with respect to the formation of salts with acids and with bases?

2. Write the equation expressing the reaction in  $\text{HNO}_3$  solution between  $\text{MnO}_2$  and bismuth peroxide, assuming the latter to be  $\text{BiO}_2$ .

3. If a permanganate were present in the original substance, what reaction would take place between it and  $\text{H}_2\text{S}$  in P. 21? Write the equation expressing it. What change in color would take place?

4. Why is a considerable excess of  $\text{NH}_4\text{OH}$  added in P. 64?

5. Explain from the mass-action standpoint why an excess of  $\text{KSCN}$  makes the iron test more delicate.

6. If  $\text{FeS}$  were treated by P. 23–30, how would it behave with each of the reagents?

**Experiment 23.**—1. Why is it necessary to test for zinc in the analysis of the iron-group?

2. Does the fact that the precipitated  $\text{NiS}$  and  $\text{CoS}$  do not dissolve in dilute  $\text{HCl}$  seem inconsistent with the behavior of nickel and cobalt in any earlier stage of the analysis? Suggest an explanation of the anomaly.

3. Why may zinc be precipitated by NaOH and  $\text{Na}_2\text{O}_2$  in the first treatment in P. 52, and yet not be precipitated by them in the second treatment in P. 67?

4. When the original  $\text{Na}_2\text{O}_2$  precipitate is so small that it need not be tested for zinc, how may P. 66-68 be simplified?

5. When the  $\text{H}_2\text{S}$  precipitate obtained in P. 66 is small, how may P. 67-68 be simplified?

6. Give the steps in the chemical process by which the precipitate of potassium cobaltinitrite may be considered to be formed.

7. Does the  $\text{NO}_2^-$  as well as the  $\text{K}^+$  coming from the excess of  $\text{KNO}_2$  diminish the solubility of the precipitate? What else, from a mass-action standpoint, might it be expected to do?

8. Give the steps in the chemical process by which in P. 70 potassium cobalticyanide may be considered to be formed.

9. What effect does the NaOBr have on this compound?

10. Describe the changes that are involved in the precipitation of  $\text{Ni}(\text{OH})_3$  in P. 70.

11. What general difference in the properties of the two elements causes the different behavior of nickel and cobalt in P. 69 and 70?

12. In the preparation of the NaOBr reagent, what is the chemical equation involved? What chemical reaction takes place in the NaOBr reagent on standing?

13. What reactions take place between NaOBr, KI, and starch, which serve to show when an excess of NaOBr is present?

14. If NiS were treated by P. 23-30, how would it behave with each of the reagents?

**Experiment 24.**—1. Why must the  $\text{HNO}_3$  be removed before testing for iron with KSCN?

2. Why does the  $\text{NH}_4\text{Ac}$  solution become red only when the quantity of iron is more than equivalent to the quantity of phosphate present?

3. What is meant by a basic salt? What are two possible simple formulas for basic ferric acetate?

**Experiment 27.**—1. What does this experiment show as to the precipitation by  $(\text{NH}_4)_2\text{CO}_3$  of magnesium and of the other alkaline-earth elements (which all behave nearly as calcium does)?

2. Why would a reagent which contained  $\text{NH}_3$  and  $\text{CO}_2$  in the molal ratio 1 : 1 not be suitable for the precipitation?

3. Why is there any advantage in adding more  $\text{NH}_3$  than corresponds to the neutral salt  $(\text{NH}_4)_2\text{CO}_3$ ?

4. If it were desired to work out a procedure for separating calcium, barium, and strontium from magnesium by means of  $(\text{NH}_4)_2\text{CO}_3$ , what experiments would one naturally make?

**Experiment 28.**—1. In order to make a separation of 1 mg. barium from 500 mg. strontium, what must be the concentration of  $\text{CrO}_4^{=}$ , stated with reference to the solubility-products of  $\text{BaCrO}_4$  and  $\text{SrCrO}_4$ ?

2. What must be true of the relative values of these two solubility-products in order that this separation may be possible?

3. Write the chemical equations for the conversion of chromate-iron into hydrochromate-ion, and for the conversion of the latter into bichromate-ion. Write also the mass-action expressions for the equilibrium of these reactions. Show by them what determines the proportion of  $\text{CrO}_4^{=}$  and of  $\text{HCrO}_4^-$  in any solution, and what determines the concentration of  $\text{Cr}_2\text{O}_7^{=}$  in any solution.

4. In practis what three substances must be added in proper proportions in order to secure the right  $\text{CrO}_4^{2-}$  concentration in the solution?

5. On addition of  $\text{NH}_4\text{OH}$  in P. 84 what chemical change causes the change in color from orange to yellow? Why from a mass-action standpoint does the addition of  $\text{NH}_4\text{OH}$  cause this change to take place? Why does this change cause strontium to precipitate?

6. Explain fully with reference to the value of the solubility-products why the oxalate-carbonate-chromate mixture used in P. 85 does not affect  $\text{BaCrO}_4$ ; why it converts  $\text{SrCrO}_4$  into  $\text{SrCO}_3$ ; and why it converts  $\text{CaCrO}_4$  into  $\text{CaC}_2\text{O}_4$ .

7. Why does  $\text{CaC}_2\text{O}_4$  dissolve in dilute  $\text{H}_2\text{SO}_4$ , but not in  $\text{HAc}$ ?

8. How does P. 87 distinguish calcium from barium and strontium, which form much less soluble sulfates? How does it distinguish calcium from magnesium?

9. Could magnesium be precipitated by any other reagent in the form of a compound closely analogous to magnesium ammonium phosphate?

10. If a flocculent precipitate obtained in P. 88 contained calcium, how might it be treated so as to remove the calcium from it and enable the usual magnesium test to be again applied?

11. If a precipitate obtained in P. 88 contained  $\text{FePO}_4$  (or  $\text{AlPO}_4$ , which behaves like it), how could the latter be separated from any  $\text{MgNH}_4\text{PO}_4$  that might also be present?

**Experiment 30.**—1. If the ammonium salt were not completely removed by the ignition, how would it behave in the subsequent test for potassium?

2. How might a solution of  $\text{Na}_3\text{Co}(\text{NO}_2)_6$  be prepared, judging from previous experience with an analogous compound?

**Experiment 32.**—1. What two things determin whether or not an acid passes over into the first distillate?

2. Show by reference to the mass-action expressions for the ionization of the two acids what determines the extent to which an acid is displaced from its salt by another acid, taking  $\text{K}^+\text{CN}^-$  and  $\text{H}^+\text{H}_2\text{PO}_4^-$  as an example.

3. Explain by reference to the mass-action expressions involved why  $\text{BaCO}_3$  dissolves on adding  $\text{HAc}$ , and why  $\text{BaSO}_3$  does not.

4. Show how phosphoric, pyrophosphoric, and metaphosphoric acids are related to one another in composition.

5. If a compound of an element forming an insoluble phosphate (for example,  $\text{CaCO}_3$ ) were distilled with  $\text{H}_3\text{PO}_4$ , would the insoluble phosphate separate in the distilling flask? Explain why or why not.

6. If  $\text{H}_2\text{SO}_3$  is found in the first distillate, which of the other substances that may be in that distillate is it unnecessary to test for? Write the equation for the reaction which would take place between  $\text{H}_2\text{SO}_3$  and each of these substances.

7. In a substance soluble in water which has been found to contain barium, which of the following constituents would it be unnecessary to test for: nitrate, phosphate, sulfide, sulfite, chloride, sulfate, carbonate?

8. Why would sulfite not be present in a mineral substance found in nature?

**Experiment 33.**—1. What different constituents of the original substance may give rise to sulfur in the distillate? what ones to sulfurous acid?

2. Why is  $\text{BaSO}_3$  readily dissolved by  $\text{HCl}$ , but scarcely at all dissolved by the  $\text{HAc}$  previously added to the first distillate?

3. Show that  $\text{H}_3\text{PO}_4$  which had been thrown over mechanically into the first distillate would not interfere with the tests for sulfite and carbonate in P. 102.

**Experiment 34.**—1. What different constituents in the original substance may give rise to chlorine in the first distillate? Write chemical equations illustrating its production from each of these constituents.

2. What different substances that might be present in the distillate would cause iodine to be set free on the addition of KI?

3. What conclusions could be drawn from the tests of the first two paragraphs of P. 103 as to the presence or absence of each of the three halogens in a distillate containing the following halogens: *a*, I<sub>2</sub>, Br<sub>2</sub>, and Cl<sub>2</sub>; *b*, Br<sub>2</sub>; *c*, Cl<sub>2</sub>; *d*, no halogen?

4. Explain why the aqueous solution must be made strongly acid with HNO<sub>3</sub> to enable the Cl<sub>2</sub> to be extracted nearly completely from it by the chloroform.

5. Write chemical equations illustrating the process by which a small quantity of HNO<sub>2</sub> liberates a large quantity of iodine from KI.

**Experiment 37.**—1. In the test for cyanide what is the purpose of adding both FeSO<sub>4</sub> and FeCl<sub>3</sub>?

2. Into what compounds is K<sub>4</sub>Fe(CN)<sub>6</sub> decomposed when it is distilled with H<sub>3</sub>PO<sub>4</sub>?

3. Referring to the results of Expt. 26 with ferrous and ferric salts, suggest how a ferrocyanide could be distinguished from a ferricyanide by tests applied to a solution of the original substance.

**Experiment 39.**—1. To what extent is the analysis of the second distillate simplified when AgNO<sub>3</sub> gives no precipitate?

2. Some H<sub>3</sub>PO<sub>4</sub> may pass over into the second distillate. Would Ag<sub>3</sub>PO<sub>4</sub>, which is only slightly soluble in water, precipitate in the AgNO<sub>3</sub> test, and thus obscure the test for the other constituents?

3. When is it necessary to test the second distillate for sulfide?

4. Explain by the mass-action principles why a sulfide may give off an appreciable quantity of H<sub>2</sub>S only in the second part of the distillation.

5. Show that Ag<sub>2</sub>S must be much more soluble in dilute HNO<sub>3</sub> than in water. Explain then why it is so slightly soluble in dilute HNO<sub>3</sub>?

6. When 2KCN are added to 1 AgNO<sub>3</sub> the compound K<sup>+</sup>Ag(CN)<sub>2</sub><sup>-</sup> forms almost quantitatively. How does this show that in the saturated solution of AgCN the salt must be present mainly as Ag<sup>+</sup> and Ag(CN)<sub>2</sub><sup>-</sup>?

**Experiment 41.**—1. What constituents in the substance are likely to give rise to chlorine in the second distillate? to iodine?

2. Explain the fact that iodine is extracted more slowly from an aqueous solution when it contains iodide. State the law that determines the quantity extracted.

3. State the principles involved in the process used for the detection of the three halides in the presence of each other.

4. Does the fact that only a very small quantity of bromine is liberated in the first step of the process mean that the reaction between the bromide and KMnO<sub>4</sub> is in equilibrium under the conditions prevailing in the solution?

5. What is meant by the statement that a reaction is in equilibrium? How would one proceed to determine whether a given reaction is in equilibrium?

6. If the mixture of KBr, NaAc, HAc, and KMnO<sub>4</sub> were allowed to stand a day or a week, what would happen?

7. If the iodine set free in the first part of the process were not completely extracted by the chloroform, how would it interfere with the test for bromide?

8. Why is H<sub>2</sub>SO<sub>3</sub> added in the last part of the process? Write the equation for the reaction which it causes.

9. Why is HNO<sub>3</sub> added with the AgNO<sub>3</sub> at the end of the process?

**Experiment 42.**—1. If the original substance contains both nitrite and nitrate, how would each of them be detected in this system of analysis?

2. If free chlorine (coming from a chlorate) were present in the second distillate, what would happen to it when treated by P. 111?

3. Iodine is not completely reduced to HI by  $\text{FeSO}_4$ , the four substances  $\text{I}_2$ , HI, ferrous salt, and ferric salt all being present in considerable quantity at equilibrium. If a solution containing  $\text{I}_2$  or HI were submitted to P. 111, what would be the result?

**Experiment 44.**—1. Why not test for boric acid in the distillates obtained in the  $\text{H}_3\text{PO}_4$  distillation?

2. What is the advantage in P. 113 of distilling the borate with  $\text{H}_2\text{SO}_4$  and  $\text{CH}_3\text{OH}$ , rather than with  $\text{H}_2\text{SO}_4$  with water?

**Experiment 45.**—1. Why must all the substances used in the test for fluoride be thoroughly dry?

2. What happens to  $\text{KHSO}_4$  when it is heated?

3. What are the main constituents of glass? What is the action of HF on it?

4. Since  $\text{H}_2\text{SiO}_3$  is non-volatile, how can the deposit be driven up the tube by heating?

5. Of what does the white deposit left after washing the tube with water consist?

6. Show why it is appropriate to call the compound  $\text{H}_2\text{SiF}_6$  "fluosilicic" acid.

7. Why is it not satisfactory to test for fluoride in the distillates obtained in the  $\text{H}_3\text{PO}_4$  distillation?

**Experiment 47.**—1. What different substances are present in the solution produced by acidifying the NaOCl solution with HAc?

2. What advantage would there be in making the hypochlorite test in alkaline solution, rather than in HAc solution? What disadvantage?

3. Assuming that the oxidation of the  $\text{PbAc}_2$  to  $\text{PbO}_2$  is caused by HOCl, but not by  $\text{Cl}_2$ , explain why the oxidation does not take place in a solution strongly acidified with  $\text{HNO}_3$ .

**Experiment 48.**—1. How may a chlorate give off chlorine in the first part of the  $\text{H}_3\text{PO}_4$  distillation? How in the second part?

2. Write the equation expressing the reaction that would take place between NaOCl and  $\text{Na}_3\text{AsO}_3$ .

3. If the hypochlorite were not reduced, AgCl and  $\text{AgClO}_3$  would be formed in the  $\text{HNO}_3$  solution by the action of the  $\text{Cl}_2$  on the  $\text{AgNO}_3$ . Write the equation expressing this reaction.

**Experiment 49.**—1. If thiosulfate were present in the original substance, what indications of it would be obtained in the first distillate? Would these distinguish it from sulfite?

2. In what case would it be essential to employ P. 118 in order to establish the presence or absence both of sulfite and thiosulfate?

3. Explain with reference to the expressions for the two solubility-products how  $\text{BaSO}_3$  can be converted into  $\text{BaCO}_3$  by treatment with  $\text{Na}_2\text{CO}_3$  solution.

4. Since  $\text{BaSO}_3$  is less soluble than  $\text{SrSO}_3$ , why not use  $\text{Ba}(\text{NO}_3)_2$  instead of  $\text{Sr}(\text{NO}_3)_2$  for the separation of sulfite and thiosulfate?

5. Where could the  $\text{BaSO}_4$  referred to in the second paragraph of P. 118 come from?

6. Assuming that the final thiosulfate test involves the equilibrium of the reaction  $\text{S}_2\text{O}_3^{2-} = \text{S} + \text{SO}_3^{2-}$ , show why a large  $\text{H}^+$  concentration should promote the separation of sulfur from the thiosulfate. (Both hydrogens of the acid  $\text{H}_2\text{S}_2\text{O}_3$ , unlike those of the acid  $\text{H}_2\text{SO}_3$ , are to a large extent dissociated.)

## PART II.

### THE SYSTEM OF ANALYSIS.

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#### PREPARATION OF THE SOLUTION.

##### PRELIMINARY EXAMINATION.

**Procedure 1.**—*Preliminary Examination.*—If the substance is a non-metallic solid, note its color, odor, and texture; examine it with a lens to determine whether it is heterogeneous, and, if so, note the appearance of its constituents. To determine whether organic matter or water is present and to get other indications, heat gently at first, then strongly, about 0.1 g. (0.1 gram) of the finely powdered substance in a hard glass tube (of about 0.6 cm. bore and 8 cm. length) closed at one end. Note whether the substance blackens, whether a tarry, aqueous, or other deposit forms on the cold part of the tube, and whether any odor is emitted. If organic matter is thus proved to be absent, pass to P. 2 (Procedure 2); if proved to be present, to P. 8.

If the substance is an alloy, treat it by P. 3.

If the substance is a solution, evaporate a measured volume of it to dryness in a small weighed dish, dry the residue thoroughly at 120–130° in a hot closet or by keeping the dish in motion over a small flame, and weigh the dish again. Heat a portion of this residue in a closed tube as described above. Treat another portion by P. 2 if organic matter is absent, or by P. 8 if organic matter is present.

*Notes.*—1. When a complete analysis in the wet way is to be made, it is usually not worth while to make a more extended preliminary examination in the dry way. The closed-tube test is, however, essential, in order to show whether organic matter is present; for certain kinds of organic matter, especially sugars and hydroxy-acids, such as tartaric, citric, and lactic acids, prevent the precipitation of the hydroxides of aluminum and chromium in the subsequent analysis, and must therefore be detected and removed. Moreover, a large quantity of organic matter of any kind interferes with the execution of the analysis; for example, with the operations of solution, filtration, and evaporation. Alloys do not contain organic matter or water; and therefore the closed-tube test need not be applied to them.

2. Blackening accompanied by a burnt odor or by the formation of a tarry deposit shows organic matter. Blackening alone does not show it; for copper, cobalt, and nickel salts may turn black on heating, owing to the formation of the black oxides.

3. It is usually desirable to determine whether water is a constituent of the substance, and, if so, whether it is present in large or small proportion. This can be done with a fair degree of delicacy by the closed-tube test, provided care be taken to keep the upper part of the tube cool during the first of the heating. Water may be present as so-called water of constitution, as in  $\text{FeO}_3\text{H}_3$  or  $\text{Na}_2\text{HPO}_4$ ; as water of crystallization, as in  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ; as enclosed water, as in some hydrated silicates like the zeolites or as mother-liquor within crystals; and as hygroscopic moisture on the surface. Water of constitution may be expelled only at a fairly high temperature, while in the other forms it is seldom retained above  $200^\circ$ .

4. The closed-tube test may also furnish evidence of the presence of certain basic and acidic constituents when they are present in considerable quantity. Thus all ammonium salts and mercury compounds are volatilized much below a red heat. Ammonium salts and the chlorides of mercury give a white sublimate. Most other mercury compounds give a gray one, consisting of minute globules of mercury, made visible by a lens or by rubbing with a wire. Metallic As,  $\text{As}_2\text{O}_3$ , and  $\text{As}_2\text{S}_3$  are also readily volatilized, forming black, white, and yellow sublimates, respectively. Of the acid-forming elements or groups, free sulfur or a persulfide is shown by a sublimate of reddish-brown drops, changing to a yellow solid on cooling, and accompanied by odor of  $\text{SO}_2$ ; a moist sulfide, by the odor of  $\text{H}_2\text{S}$ ; a nitrate or nitrite, by brown vapors of  $\text{NO}_2$ ; free iodine or a decomposable iodide, by a black sublimate of  $\text{I}_2$  and by its violet vapor; a sulfite, by the odor of  $\text{SO}_2$ ; a peroxide, chlorate, or nitrate, by evolution of oxygen, recognized by its inflaming a glowing wood-splinter held in the tube; and a carbonate or oxalate, by the evolution of  $\text{CO}_2$ , recognized by its causing turbidity in a drop of  $\text{Ba}(\text{OH})_2$  solution.

5. If the substance to be analyzed is a liquid, it is desirable to determine by evaporation how much, if any, solid substance is present in it; for enough must be taken for analysis to enable small quantities of the basic constituents to be detected. Moreover, if it is dissolved in a volatile organic solvent the latter must be removed by evaporation.



## PREPARATION OF THE SOLUTION.

TABLE I.—PREPARATION OF THE SOLUTION IN THE CASE OF NON-METALLIC SUBSTANCES.

<i>Heat the substance with water and dilute HNO<sub>3</sub> (P. 2).</i>				
<i>If it all dissolves, treat the solution by P. 11.</i>	<i>If it does not all dissolve, add more HNO<sub>3</sub>, evaporate, dry completely, add dilute HNO<sub>3</sub> (P. 3).</i>			
	<i>Solution: Treat by P. 11.</i>	<i>Residue:* a. Sb<sub>2</sub>O<sub>5</sub>, SnO<sub>2</sub>, MnO<sub>2</sub>, PbO<sub>2</sub>, HgS. b. C, Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, AgCl, CaF<sub>2</sub>, PbSO<sub>4</sub>, BaSO<sub>4</sub>, SrSO<sub>4</sub>, SiO<sub>2</sub>, and many silicates. Heat with HCl or HCl and HNO<sub>3</sub>, evaporate, add dilute HCl (P. 4).</i>		
		<i>Solution: substances under a. Treat by P. 21.</i>		
		<i>Gas: SiF<sub>4</sub>.</i>	<i>Residue: Pb, Ba, Sr, (Cr), as sulfates. Treat by P. 6.</i>	<i>Solution: other elements as sulfates. Treat by P. 11.</i>

**Procedure 2.**—*Treatment of Non-Metallic Substances Free from Organic Matter.*—Add to 1 g. of the finely powdered substance (see Note 1) in a casserole 10–30 cc. water, heat to boiling if there is a residue, and test the solution with litmus paper. (If the solution is alkaline, add to it 6-normal HNO<sub>3</sub> drop by drop till it becomes barely acid.) Add, without filtering out any residue, just 5 cc. 6-normal HNO<sub>3</sub>; and, if there is still a residue, heat the mixture to boiling. Note whether there is an odor or effervescence.

If the substance has dissolved completely, treat the solution by P. 11.

If the substance has not dissolved completely, treat the mixture, without filtering out the residue, by P. 3.

**Notes.**—1. In order that difficultly soluble substances may be dissolved, the substance must be reduced to a very fine powder. This is usually best accomplished by grinding the substance, a small quantity at a time, in a porcelain or agate mortar. With hard substances, and in general with minerals, an agate mortar should be used. As such a mortar is likely to be broken by a blow, the substance should be ground, not pounded, in it.

\* Only the more common substances that are likely to be present in the residue are here mentioned.

2. The quantity of the substance taken for analysis should always be approximately known; for a good qualitative analysis should not only show the presence or absence of the various elements in the substance, but should enable their relative quantities to be estimated. Since 1 or 2 mg. of almost any element can be detected by this system of analysis, the presence of 0.1–0.2% of an element will be detected when one gram of substance is taken, and this degree of delicacy is ordinarily sufficient. If much more than this quantity is taken, the precipitates may be so large that much time is consumed in filtering and washing them.

3. When the substance dissolves only partly in water, it is not worth while to filter off the residue and analyze it and the solution separately, unless special information in regard to the soluble constituents is desired. It is, therefore, directed to treat at once with  $\text{HNO}_3$ .

4. Just 5 cc.  $\text{HNO}_3$  must be added in order that the acid concentration may be properly adjusted in the subsequent  $\text{H}_2\text{S}$  precipitation. For the same reason, when the solution is alkaline, it must be first made nearly neutral before adding the 5 cc. of  $\text{HNO}_3$ .

5. If the aqueous solution has an alkaline reaction, the addition of an acid may cause precipitation of any substance held in solution by an alkaline solvent; for example, sulfur or sulfides of the tin group from an alkaline sulfide solution; silver chloride or cyanide from a potassium cyanide solution; silicic acid from sodium silicate solution; or basic hydroxides from solutions in alkalis. These last substances redissolve when the excess of  $\text{HNO}_3$  is added.

6. An acid reaction of the aqueous solution towards litmus is due to hydrogen-ion, which may arise from free acid, from an acid salt of a strong acid, or (by hydrolysis) from a neutral salt of a strong acid and a weak base. An alkaline reaction is due to hydroxide-ion, which may arise from a soluble hydroxide, or (by hydrolysis) from a carbonate, sulfide, phosphate, borate, cyanide, or a salt of some other weak acid.

7. When an acid is added to a nonmetallic substance or its aqueous solution, the evolution of any gas and its odor should be noted, since this indicates the nature of the acidic constituent present. Thus carbonates evolve  $\text{CO}_2$ ; sulfides,  $\text{H}_2\text{S}$ ; sulfites,  $\text{SO}_2$ ; and cyanides,  $\text{HCN}$ .

8. When the substance dissolves completely in dilute  $\text{HCl}$ , this acid may be substituted for  $\text{HNO}_3$ . It is advantageous to do this in the case of a few substances, such as  $\text{MnO}_2$ ,  $\text{Sb}_2\text{O}_5$ , and hydrated  $\text{SnO}_2$ , which dissolve in  $\text{HCl}$ , but not in  $\text{HNO}_3$ . With these substances it is best to add the  $\text{HCl}$  first, to warm till solution has taken place, and then to dilute with water and treat with  $\text{H}_2\text{S}$  by P. 21. Just 5 cc. 6-normal  $\text{HCl}$  must be added, and care must be taken to avoid loss by evaporation, as in the case of  $\text{HNO}_3$ .—As to the reasons for recommending the use of  $\text{HNO}_3$ , rather than of  $\text{HCl}$ , as the usual procedure, see Note 4, P. 3.

**Procedure 3.**—*Treatment of Non-Metallic Substances not dissolved by Dilute Nitric Acid and of Alloys.*—If the substance is non-metallic and has not dissolved in dilute  $\text{HNO}_3$ , to the mixture obtained in P. 2 add 5–10 cc.  $\text{HNO}_3$  (s.g., 1.42), and evaporate just to dryness.

If the substance is an alloy, convert it into a form offering a large surface and treat 0.5 g. of it in a casserole with 10 cc. 6-normal

$\text{HNO}_3$ . Cover the dish with a watch-glass, heat the mixture nearly to boiling as long as any action continues, adding a little  $\text{HNO}_3$  (s.g., 1.42) if action is renewed thereby, or a little water if crystalline salts have separated, and then evaporate just to dryness.

Heat the residue obtained in either case at  $120\text{--}130^\circ$  until it is perfectly dry, by keeping the casserole in motion over a small flame, or by heating it in a hot closet for half an hour. Loosen the dehydrated residue from the dish and rub it to a fine powder with a pestle; add to it just 5 cc. 6-normal  $\text{HNO}_3$ , cover the dish, and warm the mixture, taking care that none of the acid evaporates. Dilute with 20 cc. water, heat to boiling, filter, and wash the residue. (Residue, P. 4; solution, P. 11.)

*Notes.*—1. On heating the  $\text{HNO}_3$  solution, the presence of sulfides is indicated by the separation of sulfur as a spongy or pasty mass, which floats on the surface and may be removed by means of a spatula or rod; and the presence of iodides is shown by the liberation of free iodine, which may separate as a black precipitate, which imparts a brown color to the solution, and which gives rise to violet vapors above it.

2. When a silicate is decomposed by acid, silicic acid may separate as a gelatinous precipitate, but even then a part of it always remains in solution, mainly as a colloid. When thoroly dried at  $100\text{--}130^\circ$ , it is partially dehydrated and becomes entirely insoluble. The  $\text{HNO}_3$  acid solution is therefore evaporated to dryness and the residue is heated at  $120\text{--}130^\circ$ , in order to remove the silica at this point; for, if it were not removed, it would appear as a gelatinous precipitate at some later stage of the analysis; thus, if it did not separate earlier, it would be precipitated by  $\text{NH}_4\text{OH}$  together with the iron group and might then be mistaken for aluminum hydroxide. In the case of nonmetallic substances which cannot contain silica, the heating at  $120\text{--}130^\circ$  may be omitted.

3. If the substance is nonmetallic, the residue insoluble in  $\text{HNO}_3$  probably consists of one or more of the following substances: the partially dehydrated hydroxides of tin, antimony, and silicon; the native or ignited oxides of the same elements, of aluminum, and of chromium; anhydrous chromic salts; the peroxides of manganese and lead; the sulfates of barium, strontium, and lead; the sulfides of mercury and molybdenum; silica; the silicates and fluosilicates of many elements; fluoride of calcium; the halides of silver and lead; phosphate of tin; ferrocyanide of iron; sulfur; carbon; silicon carbide.

4. In dissolving nonmetallic substances  $\text{HCl}$  may be used in place of  $\text{HNO}_3$ . Each of these acids has advantages and disadvantages of its own, as follows:  $\text{HNO}_3$  dissolves, owing to its oxidizing power, many sulfides not attacked by  $\text{HCl}$ , but fails to dissolve certain oxides, especially  $\text{MnO}_2$ ,  $\text{Sb}_2\text{O}_5$ , and hydrated  $\text{SnO}_2$ , which dissolve in  $\text{HCl}$ .  $\text{HCl}$  may cause the precipitation of chlorides of the silver group; while strong  $\text{HNO}_3$  on heating oxidizes sulfides partially to sulfates, and may cause the precipitation of lead, barium, strontium, and calcium sulfates; thus in either case making it sometimes impossible to determine whether complete decomposition has resulted.  $\text{HNO}_3$  oxidizes mercurous, arsenous, antimonous, stannous, and ferrous compounds to the higher state of oxidation; consequently almost all the antimony and tin will usually be

found in the residue insoluble in dilute  $\text{HNO}_3$  after evaporation, all the mercury will be in the  $\text{H}_2\text{S}$  precipitate, and sulfur will always be precipitated by  $\text{H}_2\text{S}$  when iron is present. When  $\text{HCl}$  is used as a solvent, mercury and arsenic in the arsenous form would be wholly or partly lost, owing to the volatility of their chlorides, in the subsequent evaporation, which is necessary in order to remove silica. For this last reason, and for the reason that the procedure is a more general one in that it provides for the solution of alloys and of a larger proportion of nonmetallic substances and for the isolation of the silver group, the use of  $\text{HNO}_3$  is here recommended.

5. Alloys can not ordinarily be powdered by grinding in a porcelain or agate mortar. They may usually be converted into a form that offers a large surface by hammering in a steel mortar, filing with fine steel file, shaving with a knife, or converting into turnings with a lathe. Only 0.5 g. of an alloy is taken for analysis; for, owing to the absence of acidic constituents, the same quantity of basic elements is contained in a smaller amount of substance.

6. By the treatment of alloys with strong  $\text{HNO}_3$ , all the more common elements are dissolved by strong  $\text{HNO}_3$  except antimony, tin, and silicon. These are oxidized to antimonious acid ( $\text{Sb}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ ), metastannic acid ( $n\text{H}_2\text{SnO}_3$ ), and silicic acid ( $\text{H}_2\text{SiO}_3$ ), which separate at once as white amorphous precipitates when considerable amounts of these elements are present. Certain nitrates, especially that of lead, may separate in crystalline form from the strong  $\text{HNO}_3$ , but these dissolve upon adding water and heating to boiling.

7. In the case of an alloy the evaporation to dryness and heating at  $120$ – $130^\circ$  serve to partially dehydrate the hydroxides of silicon, tin, and antimony, whereby they are rendered nearly insoluble in  $\text{HNO}_3$ . This makes possible a conclusion in regard to their presence or absence. Thus, if after having thoroly dried the mixture at this temperature there is no residue insoluble in the  $\text{HNO}_3$ , it shows the absence of silicon and tin in quantity as large as 1 mg., and that of antimony in quantity as large as 2 or 3 mg. The fact must not be overlooked, however, that in the dehydrated form even a very small residue or slight turbidity may correspond to an appreciable quantity of one of these elements. Therefore, if no residue can be seen, rub the sides of the dish gently with the rubber-covered end of a glass rod, pour into a small flask, allow the liquid to stand 2 or 3 minutes, and note whether there is any residue whatever. The knowledge that tin is absent enables the subsequent procedures for the detection of this element to be omitted. The subsequent procedures for antimony may, in the absence of a residue, also be omitted, provided quantities as small as 3 mg. are not to be tested for. In addition to the hydroxides named above, the residue may also contain a considerable quantity of stannic phosphate or arsenate when tin and phosphorus or arsenic are simultaneously present, or of bismuth hydroxide when both antimony and bismuth are present; also small quantities of various other elements enclosed in a residue consisting of the substances already mentioned.

8. The hydroxides of antimony, tin, and silicon usually separate also in the treatment of nonmetallic substances with  $\text{HNO}_3$  when the corresponding elements are present; but the nonexistence of a residue must not, except in the case of silicon, be regarded as conclusive evidence of their absence in such substances. For the presence of certain acidic constituents, such as chloride or sulfate, may cause a considerable quantity of tin or antimony to dissolve.

9. A black or metallic residue insoluble in  $\text{HNO}_3$ , obtained in the case of an alloy, may contain carbon or carbides, certain alloys of iron, such as ferrochrome or ferrosilicon, gold, or any of the platinum metals. If there is no such residue, it shows the absence of gold and platinum.

**Procedure 4.**—*Treatment of the Residue Insoluble in Nitric Acid.*—To the residue insoluble in  $\text{HNO}_3$  (P. 3) in a casserole add gradually 5–10 cc.  $\text{HCl}$  (s.g., 1.20), and heat as long as action continues, adding more acid if necessary. If the substance does not dissolve completely in  $\text{HCl}$ , add to the mixture without filtering one-third its volume of  $\text{HNO}_3$  (s.g., 1.42), and heat gently as long as action continues, adding more of the acids if necessary.

Evaporate this solution in  $\text{HCl}$  alone, or in  $\text{HCl}$  and  $\text{HNO}_3$ , without filtering off any residue, just to dryness. Thoroughly dry the residue by heating it at  $120\text{--}130^\circ$  in a hot closet or by keeping it in motion over a small flame. Add to the residue 5 cc. 6-normal  $\text{HCl}$  measured in a small graduate, and about 20 cc. water; boil gently for a few minutes if there is a residue; filter, and wash the residue thoroughly with boiling water. Pour the filtrate into a graduate and add enough water to make its volume 100 cc. (Residue, P. 5, filtrate, P. 21.)

**Notes.**—1. Of the substances that may be present in the residue undissolved by  $\text{HNO}_3$  (see P. 3, Note 3), the peroxides of manganese and lead are reduced and dissolved by concentrated  $\text{HCl}$ ; antimonic acid, stannic phosphate, and much metastannic acid are also dissolved by it. Upon the addition of  $\text{HNO}_3$ , whereby the strongly oxidizing mixture known as *aqua regia* is produced, gold, platinum, and mercuric sulfide are entirely dissolved; and silver compounds, such as  $\text{AgBr}$ ,  $\text{AgI}$ , and  $\text{AgCN}$ , are converted into  $\text{AgCl}$ . The chloride of silver and the sulfates of strontium and lead dissolve in large quantity in the concentrated acids, but only in much smaller quantity in the small amount of dilute  $\text{HCl}$  added after the evaporation. Some of the other substances that may be in the residue, especially the oxides and certain silicates, are slowly attacked by the strong acids, but the solvent action is not rapid enough to make this a practicable method of getting them into solution.

2. The solution is evaporated to render insoluble silicic acid which may have come from the decomposition of silicates, and to remove the large quantity of acid which would otherwise interfere with the  $\text{H}_2\text{S}$  precipitation. A measured quantity of  $\text{HCl}$  is added and the solution is diluted to a definite volume, in order to produce the acid concentration required for the  $\text{H}_2\text{S}$  precipitation.

3. If the original substance was an alloy, a residue after the treatment with  $\text{HCl}$  and  $\text{HNO}_3$  is likely to consist of metastannic or silicic acid or of carbon, a platinum metal, or an alloy of iron with chromium, silicon, etc. It is best treated with  $\text{H}_2\text{SO}_4$  and  $\text{HF}$  by P. 5, in order to test for and remove silica and to dissolve metastannic acid and iron-alloys. If a black or metallic residue still remains, it may be tested for graphite by rubbing a dried portion on the fingers or on paper; and to bring it into solution the remainder may then be fused with  $\text{Na}_2\text{O}_2$  in a nickel crucible, the mass treated with water and  $\text{HCl}$ , and the solution analyzed as usual, except that nickel cannot be tested for.

4. If the original substance was an alloy and a large, nonmetallic residue remains after treatment with  $\text{HNO}_3$  (P. 3), it is sometimes advantageous, instead of treating it by P. 4, to analyze the residue separately by the following procedure, by which a large quantity of metastannic acid is more readily dissolved: Add to the residue in a casserole 3–4 cc.  $\text{H}_2\text{SO}_4$  (s.g., 1.84), and heat under the hood until the acid has evaporated to a volume of about 2 cc. Cool, add an equal volume of water, cool again, add 5 cc.  $\text{HCl}$  to dissolve antimonious oxide, and heat to boiling. Cool completely, filter if there is a residue (which may consist of silicic acid), and add the acid solution drop by drop, with constant shaking, to a mixture of 10 cc. ammonium monosulfide, 1 cc. ammonium polysulfide, and 10 cc.  $\text{NH}_4\text{OH}$  (s.g., 0.90) in a flask. Cover the flask and digest for a few minutes on a steam bath. Filter out the precipitate, which may consist of small quantities of sulfides of the copper and iron groups. Dilute the filtrate, and make it slightly acid with  $\text{HCl}$ . Shake to coagulate the precipitate, filter, and wash with hot water. Analyze the precipitate for the tin group by P. 42; reject the filtrate or test it for phosphate by P. 115.

**\*Procedure 5.—Fluoride Treatment of the Residue Insoluble in the Common Acids.**—Transfer to a platinum crucible the residue after treatment with acids (P. 4), add 2 cc.  $\text{H}_2\text{SO}_4$  (s.g., 1.84) from a graduate, heat with a moving flame until white fumes are given off, and cool completely.

To test for silicate, add carefully (see Note 1) from the loop of a platinum wire pure 40%  $\text{HF}$  drop by drop until 5–6 drops have been added, and warm the mixture over a steam bath. (Formation of gas bubbles, presence of **SILICA** or **SILICATE**.)

Then add 2–5 cc. more pure 40%  $\text{HF}$ , cover the crucible with a platinum cover, digest on a steam bath for about 15 minutes unless the residue dissolves more quickly; remove the cover and evaporate under a hood until white fumes of  $\text{H}_2\text{SO}_4$  are given off, carefully heating the sides of the crucible with a moving flame, or, better, with a ring-burner to avoid spattering. [Unless it is known from the presence of solid substance at this point or from other indications that the residue treated with  $\text{H}_2\text{SO}_4$  and  $\text{HF}$  contained other constituents than silica, determine this by evaporating off the  $\text{H}_2\text{SO}_4$  under a hood, taking care not to ignite the dry residue. If a significant residue remains, add from a graduate 1.5 cc.  $\text{H}_2\text{SO}_4$  (s.g., 1.84), and heat until the residue is redissolved, not allowing the acid to evaporate.] Cool, pour the contents of the crucible into 10 cc. water, and rinse out the contents with a little water. Boil to dissolve slowly dissolving sulfates; cool, shake, filter, and wash the residue, first with 6-normal  $\text{H}_2\text{SO}_4$  and then with a little water. (Residue, P. 6; filtrate, P. 11.)

\* If the use of a platinum crucible or of hydrofluoric acid is impracticable, the less dangerous, but less satisfactory, alternative method described in P. 7 may be employed (see Note 6, P. 5).

*Notes.*—1. A student using this procedure for the first time should work under the direct supervision of an instructor. Great care must be taken not to breathe the fumes of HF nor to get it on the hands; for it is extremely irritating and produces dangerous burns.

2. The test for silica or silicate depends on the formation of  $\text{SiF}_4$  gas, which is insoluble in strong  $\text{H}_2\text{SO}_4$ , but dissolves in water in the presence of HF with formation of fluosilicic acid,  $\text{H}_2\text{SiF}_6$ . With free silica the evolution of gas takes place in the cold; but with slowly decomposing silicates, such as feldspar, the test is obtained only upon warming. A few silicates are not acted upon by HF and  $\text{H}_2\text{SO}_4$ , and, of course, do not show the test for silica at this point. The test is delicate enough to enable 1 mg. of silica, whether free or in a decomposable silicate, to be detected. Moreover, after the substance has been treated with acids as in P. 4 and warmed with  $\text{H}_2\text{SO}_4$ , an evolution of gas with HF is not produced with the compounds of any element other than silicon. It should be borne in mind that a small quantity of silica will be introduced if ordinary filters (which have not been washed with HF) have been employed and have been destroyed by acids or by ignition, or if a strongly alkaline solution has been boiled in glass vessels, or if a substance has been fused with sodium carbonate in a porcelain crucible.

3. Since glass and porcelain consist of silicates which are readily attacked by HF, this acid must not be allowed to come into contact with these materials. In handling cold HF solutions, vessels and funnels of celluloid or paraffin or of glass coated with paraffin may be used; but platinum vessels must be employed when the solutions are to be heated. Care must be taken not to introduce into a platinum vessel any solution containing chlorine or bromine or any acid mixture containing nitrates and chlorides by which chlorine would be evolved. Platinum is so slowly attacked by hot concentrated  $\text{H}_2\text{SO}_4$  that even when 2–3 cc. of the acid are rapidly evaporated in a crucible less than 0.5 mg. passes into solution.

4. The digestion with HF decomposes most silicates and dissolves silica. The subsequent evaporation with  $\text{H}_2\text{SO}_4$  expels the excess of HF and decomposes the fluorides produced, as well as some other substances that may have been left undissolved by the  $\text{HNO}_3$  and HCl. The  $\text{H}_2\text{SO}_4$  solution is diluted with a small quantity of water so as to cause the complete precipitation of  $\text{BaSO}_4$ ,  $\text{SrSO}_4$ , and  $\text{PbSO}_4$ . These sulfates are moderately soluble in strong  $\text{H}_2\text{SO}_4$  and may not appear till after dilution. The addition of much water is avoided, since  $\text{SrSO}_4$  and  $\text{PbSO}_4$  are somewhat soluble in water; and the residue is washed with dilute  $\text{H}_2\text{SO}_4$  for the same reason. The solution is boiled so as to dissolve anhydrous sulfates, such as those of aluminum and iron.

5. The residue insoluble in dilute  $\text{H}_2\text{SO}_4$  contains as sulfates all the barium, strontium, and lead, and all of the calcium in excess of 5–10 mg., left undissolved by  $\text{HNO}_3$  and HCl; more or less of the chromium (according as the  $\text{H}_2\text{SO}_4$  has been more or less strongly heated) as a pink anhydrous sulfate; and part of the bismuth as basic sulfate and antimony as antimonie hydroxide, when much of these elements was left undissolved by the previous treatments with acids. The residue may also contain still undecomposed substances, especially the following: silver chloride; corundum,  $\text{Al}_2\text{O}_3$ ; chromite,  $\text{FeCr}_2\text{O}_4$ ; cassiterite,  $\text{SnO}_2$ ; some anhydrous silicates and fluosilicates, such as cyanite or andalusite ( $\text{Al}_2\text{SiO}_5$ ) and tourmalin; graphite and carbides; and certain compounds of the rarer elements.



6. If the use of a platinum crucible or of hydrofluoric acid is impracticable, the residue insoluble in  $\text{HCl}$  and  $\text{HNO}_3$  may be fused in a porcelain crucible with a mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ , as described in P. 7, instead of being treated by P. 5-6. This is, however, a far less satisfactory method of analysis for the following reasons. Compounds of the alkali elements are used as a flux, and aluminum, calcium, and silica are introduced from the porcelain crucible, so that these elements can not be tested for in the subsequent analysis. Moreover, the treatment with  $\text{HF}$  and  $\text{H}_2\text{SO}_4$  is almost always a shorter process, since when the residue consists only of silica, as is often the case with minerals, no further treatment is necessary, and since in other cases there is often no residue to be boiled with  $\text{Na}_2\text{CO}_3$  solution (P. 6). A fusion in a platinum crucible with alkali-metal carbonate would be less objectionable; but this is not possible, unless reducible metals are known to be absent in the residue (see Note 5, P. 7).

**Procedure 6.**—*Treatment of the Residue from the Fluoride Treatment.*—Transfer the residue insoluble in dilute  $\text{H}_2\text{SO}_4$  (P. 5) to a casserole, add about 25 cc. saturated  $\text{Na}_2\text{CO}_3$  solution, cover the casserole, and boil gently for 10 minutes. Filter and wash the residue thoroly. (Filtrate, reject.) Heat the residue with just 5 cc.  $\text{HNO}_3$  and 10-20 cc. water. Filter out any undissolved residue, and treat the solution by P. 11, subsequently testing it only for lead, bismuth, chromium, barium, strontium, and calcium.

*Notes.*—1. The boiling with  $\text{Na}_2\text{CO}_3$  converts into carbonates the sulfates of lead, calcium, strontium, and bismuth completely, and at least 80% of the sulfate of barium, even when large quantities of them are present. A second treatment, which should be applied to the residue if there are indications that barium is present, completely decomposes  $\text{BaSO}_4$ . The carbonates dissolve readily in  $\text{HNO}_3$ . Anhydrous chromic sulfate, which is left undissolved by dilute  $\text{H}_2\text{SO}_4$  (P. 5) as a fine pink or gray powder, is slowly changed by boiling with  $\text{Na}_2\text{CO}_3$  to a greenish blue hydroxide which dissolves in the  $\text{HNO}_3$ , leaving behind the still undecomposed sulfate. Antimonic oxide dissolves only to a small extent (2-4 mg.) in the  $\text{Na}_2\text{CO}_3$  solution or in the dilute  $\text{HNO}_3$ .

2. Any residue insoluble in  $\text{HNO}_3$  can therefore consist only of barium or chromic sulfate, of antimonie oxide, or of some of the original substance still undecomposed, which is likely to consist of one of the native oxides or silicates mentioned in P. 5, Note 5. If such a residue is obtained, it can ordinarily be rendered soluble by fusion with  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ , and  $\text{KNO}_3$ , as described in P. 7; but in this case a platinum crucible may be used for the fusion, provided the residue be first heated with  $\text{HCl}$  to extract any  $\text{Sb}_2\text{O}_5$  that may be present and provided silver is not found present in the  $\text{H}_2\text{SO}_4$  solution obtained in P. 5.

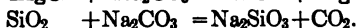
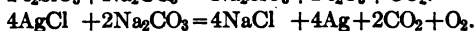
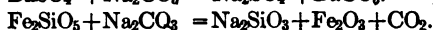
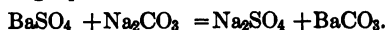
**Procedure 7.**—*Alternative Treatment of the Residue Insoluble in the Common Acids.*—If the use of  $\text{HF}$  (P. 5) is impracticable, transfer the residue insoluble in acids (P. 4), with the filter if necessary, to a porcelain crucible, heat until the residue is dry or until the filter is destroyed, mix the residue, which must be very finely divided, with

ten to twenty times its weight of a mixture of anhydrous  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ , cover the crucible, heat strongly over a powerful burner so that complete fusion takes place, and continue the heating for 10–20 minutes. If dark particles of undecomposed substance can still be seen, add gradually in small portions 0.1–0.5 g. of solid  $\text{KNO}_3$ , and heat strongly for several minutes. Cool, boil the crucible and its contents with water until the fused mass is disintegrated, filter, and wash the residue thoroly. Warm the residue with  $\text{HNO}_3$  until action ceases, and filter out any still undecomposed substance. Mix a small part of the  $\text{HNO}_3$  solution with a small part of the carbonate solution, making the mixture strongly acid with  $\text{HNO}_3$ , if it is not already so.

If no precipitate forms, mix the remainder of the acid solution with the remainder of the carbonate solution. Add 3–5 cc.  $\text{HCl}$  (or more if the solution is still alkaline), and filter. Test the precipitate for silver and lead by P. 12. Evaporate the solution, and heat the residue until it is thoroly dry at 120–130° in a hot closet or by keeping it in motion over a small flame. Add from a graduate just 5 cc. 6-normal  $\text{HNO}_3$  and about 20 cc. water, and heat to boiling. Filter out any residue (see Note 2), dilute the filtrate to 100 cc., and treat it by P. 21.

If a precipitate forms on mixing the small portions of the  $\text{HNO}_3$  solution and the carbonate solution, treat these solutions separately as described in the preceding paragraph, uniting the precipitates formed by the same group reagent in the subsequent analysis.

*Notes.*—1. Upon fusion with sodium carbonate most compounds undergo metathesis, the acidic constituent of the compound combining with the sodium, and the basic element with the carbonate. The carbonate formed is, however, sometimes decomposed by heat with production of the oxide or of the metal itself. Acid-forming oxides, such as  $\text{SiO}_2$ ,  $\text{As}_2\text{O}_5$ , and less rapidly  $\text{Al}_2\text{O}_3$ , expel  $\text{CO}_2$  from the carbonate and form sodium salts. Such reactions are illustrated by the following equations:



After the treatment with water, the acidic constituent of the substance is therefore found with the excess of carbonate in the aqueous extract, while the basic element remains undissolved by the water and passes into the acid solution. The first and third reactions are examples of cases where the aqueous and acid solutions must not be mixed, for upon mixing  $\text{BaSO}_4$  or  $\text{AgCl}$  would again be formed.

2. Of the basic elements that may be present, all or a part of the arsenic, antimony, tin, aluminum, chromium and manganese are contained in the

carbonate solution; and this solution must therefore be analyzed for basic elements. Since this solution may also contain  $\text{Na}_2\text{SiO}_3$ , the solution after the addition of acid is evaporated to dryness, and the residue is heated at  $120\text{--}130^\circ$ , in order to dehydrate the silicic acid and render it insoluble. The residue insoluble in  $\text{HNO}_3$  after this treatment usually consists only of silicic acid. To prove whether it consists wholly of this acid, it may be treated with  $\text{H}_2\text{SO}_4$  and  $\text{HF}$  as described in P. 5.

3. Some substances which are not much acted upon by alkali carbonates alone are readily attacked when an oxidizing substance like  $\text{KNO}_3$  is present. Thus, sulfides are converted into sulfates and chromium compounds (such as chromite,  $\text{FeOCr}_2\text{O}_3$ ) into chromates. A few substances, however, such as the nativ or ignited oxides of tin and aluminum, may be only partially decomposed even by long-continued fusion with the mixed fluxes. Such an undecomposed residue may be fused with  $\text{KOH}$  in a nickel or silver crucible and the fusion treated first with water and then with  $\text{HCl}$ . The oxides of aluminum and stannic tin, if finely powdered, dissolve rapidly in fused  $\text{KOH}$ . The aqueous extract contains the aluminum as aluminate and most of the tin as stannate. The residue undissolved by water may consist of black nickel oxide from the crucible, stannic hydroxide, and of other hydroxides accompanying the aluminum or tin oxides; all of which dissolve in  $\text{HCl}$ .

4. Aluminum, calcium, and silica are taken up from the porcelain crucible by the flux, so that these elements, as well as the alkali elements, cannot be tested for later in the analysis. The crucible is, moreover, so attacked by the flux that it cannot well be used for a second fusion.

5. Whenever it is permissible, it is therefore better to make the fusion in a platinum crucible, since then no foreign substances are introduced from the crucible. It is not permissible, however, to heat in platinum compounds of the elements of the silver, copper, and tin groups that may be reduced to the metal by heating with an alkaline flux. The same is true of sulfur, sulfides, and in the presence of organic matter of phosphates; for all these elements form easily fusible alloys with the platinum, and thus spoil the crucible. Moreover, alkaline hydroxides and strongly oxidizing fluxes (such as peroxides and nitrates) must not be fused in platinum, since they attack it fairly rapidly. Therefore, if the fusion is made in platinum, no more  $\text{KNO}_3$  should be added than is necessary.

6. If platinum is not available, or if it is not known that reducible elements are absent, a pure nickel crucible can be used with advantage in place of the porcelain one. This enables aluminum, calcium, and silica to be tested for. Some nickel, but only a few milligrams, will then be found in the acid solution of the fusion. Reducible elements, if present, would alloy with the nickel, but the destruction of a crucible of this cheap material is not of much consequence. Ordinarily a nickel crucible can be used repeatedly.

**Procedure 8.—Destruction of Organic Matter.**—If the closed-tube test (P. 1) has shown the presence of organic matter, powder, or cut into small pieces, 1–5 g. of the substance (according to the quantity of organic matter present). Add to it in a casserole about 5 cc.  $\text{H}_2\text{SO}_4$  (s.g., 1.84); warm gently until the substance is well charred; cool; add slowly, with constant stirring, under a hood,  $\text{HNO}_3$  (s.g.,

1.42), until violent reaction ceases; digest for a few minutes on a steam bath, and then heat over a flame, keeping the dish moving, until the substance is thoroly charred. Cool, again add  $\text{HNO}_3$  (s.g., 1.42) as before, and heat until thick fumes of  $\text{H}_2\text{SO}_4$  are evolved; cool somewhat, and add a little  $\text{HNO}_3$ . Repeat this process till the mixture becomes light-colored and remains so when heated strongly.

If the substance has dissolved completely (or even if it has not, if the use of  $\text{HF}$  is impracticable), evaporate off the  $\text{H}_2\text{SO}_4$  under a hood till only 1.5 cc. remains, cool completely, add very carefully 10–20 cc. water, and boil. (If a precipitate separates, filter it off and treat it by P. 6.) Treat the solution by P. 11.

If the substance has not dissolved completely, transfer the mixture to a platinum crucible, evaporate off the  $\text{H}_2\text{SO}_4$  till only 1.5 cc. remain, cool completely, and treat the mixture by the second and third paragraphs of P. 5.

*Notes.*—1. This method of destroying organic matter is of very general application, being effective even when such stable substances as paraffin and cellulose are present. Organic matter can also be destroyed by ignition, but this has the disadvantages of volatilizing certain elements, especially mercury and arsenic, and of making some substances very difficultly soluble. When the organic matter consists only of oil, as is the case with an oil paint, it may be better to extract it with ether, especially when it is desired to determine the proximate constituents of the substance.

2. The residue contains: any substances originally present that have not been attacked by  $\text{HNO}_3$  or  $\text{H}_2\text{SO}_4$ , especially silicates; all the lead, strontium, and barium that may have been present in any form, since the sulfates of these elements are insoluble in dilute  $\text{H}_2\text{SO}_4$ ; all the silica, since silicic acid is dehydrated and made insoluble by heating with  $\text{H}_2\text{SO}_4$ ; some of the calcium, bismuth, antimony, and tin, when these elements are present in considerable quantity, since their sulfates (or oxides) are not readily soluble in dilute  $\text{H}_2\text{SO}_4$ ; and substantially all of the chromium, since its sulfate is converted into the insoluble anhydrous form.

3. After the organic matter is destroyed, the solution is evaporated to 1.5 cc., in order that the concentration of the acid may be properly adjusted in the subsequent  $\text{H}_2\text{S}$  precipitation.

## DETECTION OF THE BASIC CONSTITUENTS.

TABLE II.—DIVISION OF THE BASIC ELEMENTS INTO GROUPS.

SOLUTION IN DILUTE NITRIC ACID CONTAINING ALL THE COMMON BASIC ELEMENTS. Add $\text{NH}_4\text{Cl}$ (P. 11).				
Precipitate: SILVER-GROUP (Pb, * Ag, Hg*), as chlorides. See Table III.	Filtrate. Saturate with $\text{H}_2\text{S}$ gas (P. 21).			
	Precipitate: COPPER-GROUP and TIN-GROUP as sulfides. Treat with $(\text{NH}_4)_2\text{S}_x$ (P. 22).		Filtrate: Add $\text{NH}_4\text{OH}$ and $(\text{NH}_4)_2\text{S}$ (P. 51).	
	Residue: COPPER-GROUP (Hg, Pb, Bi, Cu, Cd), as sulfides. See Table IV.	Solution: TIN-GROUP (As, Sb, Sn), as sulfo-salts. See Table V.	Precipitate: ALUMINUM-GROUP and IRON- GROUP, as hydroxides and sulfides. Dissolve in acid, add $\text{NaOH}$ and $\text{Na}_2\text{O}_2$ (P. 52).	
			Filtrate: ALUMINUM-GROUP (Al, Cr, Zn), as sodium salts. See Table VI.	Precipitate: IRON-GROUP (Mn, Fe, Co, Ni), as hydroxides. See Table VII.
			Precipitate: ALKALINE- EARTH-GROUP (Ba, Sr, Ca, Mg), as carbonates. See Table VIII.	Filtrate: ALKALI- GROUP ( $\text{NH}_4$ , K, Na), as nitrates, etc. See Table IX.

\* Lead is precipitated with the silver-group only when a large quantity is present, and then only partially; mercury is precipitated only when it is in the mercurous state.

## PRECIPITATION AND ANALYSIS OF THE SILVER-GROUP.

TABLE III.—ANALYSIS OF THE SILVER-GROUP.

Precipitate: $\text{AgCl}, \text{Hg}_2\text{Cl}_2, \text{PbCl}_2$ . <i>Treat with hot water (P. 12).</i>		
Solution: $\text{PbCl}_2$ . Add $\text{H}_2\text{SO}_4$ (P. 13).	Residue: $\text{AgCl}, \text{Hg}_2\text{Cl}_2$ . <i>Pour <math>\text{NH}_4\text{OH}</math> through the filter (P. 15).</i>	
Precipitate: $\text{PbSO}_4$ . <i>Dissolve in <math>\text{NH}_4\text{Ac}</math>, add <math>\text{K}_2\text{CrO}_4</math> (P. 14).</i>	Black Residue: $\text{HgNH}_2\text{Cl} + \text{Hg}$ .	Solution: $\text{Ag}(\text{NH}_3)_2\text{Cl}$ . Add $\text{HNO}_3$ (P. 15).
Yellow precipitate: $\text{PbCrO}_4$ .		White precipitate: $\text{AgCl}$ .

**Procedure 11.**—*Precipitation of the Silver-Group.*—To the cold acid solution of the substance (P. 2, 3, 5, 6, or 8) contained in a conical flask, add 10 cc.  $\text{NH}_4\text{Cl}$  solution. (White precipitate, presence of SILVER-GROUP.) Filter, and wash the precipitate with a small quantity of cold water, adding the washings to the filtrate. (Precipitate, P. 12; filtrate, P. 21.)

*Notes.*—1. It is recommended that in general hard-glass conical flasks (the so-called Erlenmeyer flasks of Jena or Bohemian glass), rather than beakers or test-tubes, be employed for holding solutions that are being subjected to the operations of precipitation and heating.

2. Even in cases where it is not essential to add a perfectly definite volume of a reagent, the analyst should make it a practice to measure out the quantity to be added, rather than to pour in an indefinite quantity from the reagent bottle. For this purpose a 10 cc. graduate should be constantly at hand. For adding smaller quantities than 1 cc. a dropper should be used. This may be made by drawing out one end of a short glass tube to a wide capillary and capping the other end with a rubber nipple.

3. Unless the concentration is specified, it is understood that all salt solutions used as reagents are 1-normal; that is, that they contain one equivalent of salt per liter of solution.

4. If  $\text{NH}_4\text{Cl}$  produces no precipitate, it proves the absence of silver and mercurous mercury, but not of lead, since  $\text{PbCl}_2$  is fairly soluble in water. Its solubility is greatly decreased by the addition of  $\text{NH}_4\text{Cl}$ ; but a considerable quantity of lead may remain in solution, and thus escape detection in this group. On account of the considerable solubility of  $\text{PbCl}_2$  the precipitate is washed with only a little cold water, and in this case, contrary to the usual practice, the washings are added to the filtrate.

**Procedure 12.**—*Extraction of the Lead with Boiling Water.*—Pour repeatedly through the filter containing the  $\text{NH}_4\text{Cl}$  precipitate (P. 11) a portion of 10–20 cc. boiling water. Wash the residue thoroly with hot water. (Residue, P. 15; solution, P. 13.)

**Procedure 13.—Precipitation of Lead with Sulfuric Acid.**—Add to the aqueous extract from the  $\text{NH}_4\text{Cl}$  precipitate (P. 12) one-fifth its volume of  $\text{H}_2\text{SO}_4$  (s.g., 1.84); cool, shake the mixture, and allow it to stand for 5 minutes. (White precipitate, presence of LEAD.) Filter, wash the precipitate with 6-normal  $\text{H}_2\text{SO}_4$ , and then with a little water. (Precipitate, P. 14; filtrate, reject.)

*Note.*— $\text{PbSO}_4$  is slightly soluble in water, but much less so in dilute  $\text{H}_2\text{SO}_4$ ; hence  $\text{H}_2\text{SO}_4$  is added in excess to the solution and 6-normal  $\text{H}_2\text{SO}_4$  is used for washing the precipitate.

**Procedure 14.—Confirmatory Test for Lead.**—Pour repeatedly through the filter containing the  $\text{H}_2\text{SO}_4$  precipitate (P. 13) a 5–20 cc. portion of  $\text{NH}_4\text{Ac}$  solution; add to the filtrate a few drops  $\text{K}_2\text{CrO}_4$  solution and 2–5 cc.  $\text{HAc}$ . (Yellow precipitate, presence of LEAD.)

*Notes.*—1. When it is directed to add  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HAc}$ ,  $\text{NH}_4\text{OH}$ , or  $\text{NaOH}$  without specifying the specific gravity or concentration, the ordinary reagent consisting of the 6-normal acid or base should be employed.

2. Whenever two quite different limiting quantities of the reagent are specified (for example, 5–20 cc. as in this procedure), the quantity added should be adjusted to the size of the precipitate.

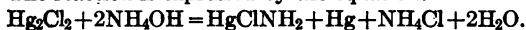
3. The symbol  $\text{Ac}$  is used throughout this book to denote the acetate-radical ( $\text{C}_2\text{H}_3\text{O}_2$ ). Thus  $\text{NH}_4\text{Ac}$  denotes ammonium acetate;  $\text{HAc}$ , acetic acid.

4. The solubility of  $\text{PbSO}_4$  in  $\text{NH}_4\text{Ac}$  solution depends on the formation by metathesis of undissociated  $\text{PbAc}_2$ , which is much less ionized than most other salts of the same type. On the addition of a chromate to this solution the much more difficultly soluble  $\text{PbCrO}_4$  is precipitated.

5. This confirmatory test distinguishes  $\text{PbSO}_4$  from the difficultly soluble sulfates of barium, strontium, and calcium, since the chromates of all of these are more soluble than the sulfates.

**Procedure 15.—Detection of Silver and Mercury.**—Pour repeatedly through the filter containing the residue insoluble in hot water (P. 12) a 10–20 cc. portion of  $\text{NH}_4\text{OH}$ . (Black residue on the filter, presence of MERCUROUS MERCURY.) Acidify the filtrate with  $\text{HNO}_3$ . (White precipitate, presence of SILVER.)

*Notes.*—1. The black residue produced by the action of  $\text{NH}_4\text{OH}$  on  $\text{Hg}_2\text{Cl}_2$  is a mixture of finely divided mercury with the white mercuric compound  $\text{HgClNH}_2$ . The reaction is expressed by the equation:



The compound  $\text{HgClNH}_2$  may be considered to be a derivative of  $\text{HgCl}_2$ , formed by replacing an atom of chlorine by the univalent radical  $\text{NH}_2$ .

2. An  $\text{NH}_4\text{OH}$  solution contains a considerable proportion of (unhydrated)  $\text{NH}_3$ , and  $\text{AgCl}$  dissolves readily in it, owing to the formation of a soluble complex salt,  $\text{Ag}(\text{NH}_3)_2\text{Cl}$ , which in solution is largely ionized into  $\text{Ag}(\text{NH}_3)_2^+$  and  $\text{Cl}^-$  ions. This complex cation has so slight a tendency to dissociate into  $\text{Ag}^+$  and  $\text{NH}_3$  that the ratio of its concentration to that of the simple  $\text{Ag}^+$  ion is about  $10^7$  in a normal solution of  $\text{NH}_4\text{OH}$ .

## PRECIPITATION AND SEPARATION OF THE COPPER AND TIN GROUPS.

See Table II, Page 34.

**Procedure 21.**—*Precipitation of the Copper and Tin Groups.*—Dilute to 100 cc. the filtrate from the  $\text{NH}_4\text{Cl}$  precipitate (P. 11) or the solution of the substance in  $\text{HCl}$  (P. 4), which should contain just 5 cc. of 6-normal  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , or  $\text{HCl}$ . Place this solution in a conical flask provided with a two-hole rubber stopper in which is a tube leading to the bottom of the flask. Pass into it in the cold a slow current of  $\text{H}_2\text{S}$ , until, upon shutting off the gas and shaking thoroly, the liquid smells strongly of  $\text{H}_2\text{S}$ . Filter at once, wash the precipitate with hot water (see Note 1), and treat it by P. 22. Heat the filtrate nearly to boiling (to  $70\text{--}90^\circ$ ), and pass  $\text{H}_2\text{S}$  into it at that temperature for 5–10 minutes.

If there is no further precipitate, treat the solution by P. 51.

If there is a further precipitate, boil the solution till it no longer smells of  $\text{H}_2\text{S}$ , filter out the precipitate, and evaporate the solution almost to dryness. Add 3–5 cc.  $\text{HCl}$  (s.g., 1.20) and evaporate just to dryness (see Note 2), to destroy the  $\text{HNO}_3$ . Then add 10–15 cc. 6-normal  $\text{HCl}$ , saturate the cold solution with  $\text{H}_2\text{S}$ , heat it to  $70\text{--}90^\circ$ , and pass  $\text{H}_2\text{S}$  into it for 5–10 minutes. Filter out the precipitate, collecting it with that previously obtained from the hot solution; wash it, and test it for arsenic by P. 43. Treat the filtrate by P. 51.

*Notes.*—1. The washing of precipitates should in general be continued until the wash-water will no longer give a test for any substance known to be present in the filtrate (for example, in this case for acid with blue litmus-paper or for chloride with  $\text{AgNO}_3$ ). Precipitates which are practically insoluble in water (like all the sulfides and hydroxides that are met with in this System of Analysis) are best washed with nearly boiling water as this runs through the filter more rapidly and extracts soluble substances more readily. Precipitates which are appreciably soluble should be washed with cold water and with only a small quantity of it. The wash-water should in general not be allowed to run into the filtrate, so as not to dilute it unnecessarily. When, however, a considerable proportion of the solution is likely to be retained in the filter and precipitate, it is well to add the first washings to the filtrate.

2. When it is directed, as in the last part of this procedure, to evaporate a solution just to dryness, this should be done on a steam-bath or by keeping the dish moving over a small flame in such a way as not to overheat the residue.

3. The formation of a white or yellowish precipitate which immediately turns black with more  $\text{H}_2\text{S}$  indicates mercury. (The white compound is  $\text{HgCl}_2 \cdot 2\text{HgS}$ , and this is converted into  $\text{HgS}$  by the excess of  $\text{H}_2\text{S}$ .) An orange precipitate shows antimony; a yellow one, cadmium, arsenic, or stannic tin. All the other sulfides are black.



4. The acid concentration is made 0.3 normal (5 cc. of 6-normal acid being present in 100 cc.) and the solution is saturated with  $H_2S$  gas in the cold, since under these conditions even 1 mg. of cadmium, lead, or tin precipitates, and even 300 mg. of zinc remain in solution. This statement in regard to zinc is true, however, only when the solution contains also a considerable quantity of chloride-ion, such as was added in P. 11, and when it is not allowed to stand.

5. The solution is afterwards heated nearly to boiling and again saturated with  $H_2S$ , in order to ensure the detection of arsenic; for this element, when present in the higher state of oxidation (as arsenic acid) is only very slowly precipitated by  $H_2S$  in the cold. At  $70-90^\circ$  the precipitation is much more rapid, especially if the solution has been previously saturated with  $H_2S$  in the cold. Under these conditions even 1 mg. As gives a distinct precipitate in less than 5 minutes. Continuous treatment with  $H_2S$  at  $70-90^\circ$  in an open vessel does not, however, completely precipitate a large quantity of arsenic from such a weakly acid solution even within an hour. For this reason, when a considerable precipitate forms in the hot solution, it is directed to evaporate the filtrate, to add  $HCl$  to destroy the  $HNO_3$  (which in the concentrated state would decompose the  $H_2S$ ), to dissolve the residue in  $HCl$ , and to pass  $H_2S$  through the hot solution. From this concentrated acid solution the arsenic precipitates completely in 5-10 minutes. The reasons for this peculiar behavior of arsenic in the higher state of oxidation are presented in Note 2, P. 44.

6. The effect of acid on the precipitation of the sulfides is explained by the mass-action law and ionic theory as follows: When a dilute solution, whether aqueous or acid, is saturated at a definite temperature with  $H_2S$  gas under the atmospheric (or any definite) pressure the  $H_2S$  present as such always has the same concentration. This ionizes, however, to a slight extent into  $H^+$  and  $HS^-$ , and to a still less extent into  $2H^+$  and  $S^{2-}$ . It is only the latter form of ionization that needs to be considered here. Now between the  $H_2S$  and its ions must be maintained the equilibrium expressed by the equation\*  $(H^+)^2 \times (S^{2-}) = \text{const.} \times (H_2S)$ ; or, since in this case  $(H_2S) = \text{const.}$ , as just stated, it follows that also  $(H^+)^2 \times (S^{2-}) = \text{const.}$  From this it is evident that when  $(H^+)$  is increased by the addition of acid to the solution,  $(S^{2-})$  must be decreased in the proportion in which the square of  $(H^+)$  is increased; thus, if  $(H^+)$  is doubled,  $(S^{2-})$  will be reduced to one-fourth. But in order that a sulfide—for example, of the formula  $M^{++}S^{2-}$ —may precipitate, the concentration-product  $(M^{++}) \times (S^{2-})$  must attain a value equal to the solubility-product, which is the value of this concentration product which prevails in pure water in contact with the solid sulfide. The solubility-product varies, however, with the nature of the sulfide and with the temperature; and therefore the acid concentration that will barely permit of precipitation when  $(M^{++})$  has a definite value (for example, 1 mg. in 100 cc.) will be different for different sulfides and for the same sulfide at different temperatures. Thus if the elements are arranged in the order in which they are precipitated from cold  $HCl$  solutions as the acid-concentration is progressively decreased, the series is approximately as follows: arsenic, mercury and copper, antimony, bismuth and stannic tin, cadmium, lead and stannous tin, zinc, iron, nickel and cobalt, manganese. The acid concentration which permits precipitation also varies

\* In mass-action expressions of this kind, chemical formulas within parentheses denote the concentrations of the respective substances.

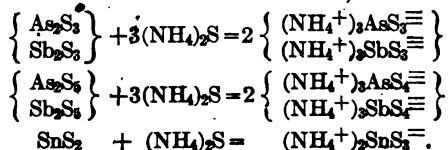
with the ionization of the acid; thus zinc is precipitated from a fairly concentrated solution of acetic acid, since, owing to the slight ionization of this acid, the  $H^+$  concentration is less than in a far more dilute solution of HCl. The three acids, HCl,  $HNO_3$ , and  $H_2SO_4$ , do not, however, differ greatly in this respect, since they are all largely ionized in dilute solution.

7. A white, finely divided precipitate of free sulfur will be formed if the solution contains substances capable of oxidizing  $H_2S$ . The most important of these likely to be present are ferric salts, chromates, permanganates, and chlorates. The reduction by  $H_2S$  of ferric salts to ferrous is attended by a change in color from yellow to colorless; of chromates to chromic salts, from orange to green; and of permanganates to manganous salts, from purple to colorless. Nitric acid, if it were fairly concentrated, would also destroy the  $H_2S$ ; but at the concentration in question (0.3 normal) it has scarcely any oxidizing action even in boiling solution.

8. When an oxidizing substance is present, some of the  $H_2S$  is oxidized to  $H_2SO_4$ . Barium, if present, may then be precipitated as  $BaSO_4$  so completely that not more than 1-2 mg. remain in solution. Provision is therefore made for detecting barium in the analysis of the copper-group (see P. 26, Note).

**Procedure 22.**—*Separation of the Copper and Tin Groups by Ammonium Sulfide.*—Transfer the  $H_2S$  precipitate (P. 21) to a small casserole, add to it 10-25 cc. ammonium monosulfide (if the original substance was treated with strong  $HNO_3$  in P. 3), or 5-10 cc. ammonium polysulfide (if it was dissolved in water or in dilute  $HNO_3$  in P. 3), cover the dish, and warm the mixture slightly (to 40-60°) for about 10 minutes with frequent stirring. Add 10 cc. water, filter, and wash once with hot water. [If the residue is large and much has been extracted from it by this treatment, as indicated by its appearance or as determined in P. 41, warm it again with ammonium monosulfide or polysulfide, and filter, collecting the filtrate separate from the first one.] Wash the residue thoroly with hot water (or, in case the precipitate tends to pass through the filter, with hot water containing about 5%  $NH_4NO_3$ ), not adding the washings to the filtrate. (Residue P. 23; solutions, P. 41.)

**Notes.**—1. The action of ammonium sulfide in dissolving the sulfides of the tin-group depends on the formation of soluble salts of sulfoacids with complex anions. When the monosulfide is used, the reactions are as follows:



The excess of sulfur in the polysulfide oxidizes the lower sulfides ( $As_2S_3$ ,  $Sb_2S_3$ ,  $SnS$ ) to the same sulfoacids as are obtained by dissolving the higher sulfides ( $As_2S_5$ ,  $Sb_2S_5$ ,  $SnS_2$ ) in ammonium monosulfide. It will be seen that these sulfo-salts are analogous to the salts of the familiar oxygen acids of these ele-

ments, the difference being that sulfur has replaced oxygen; and they are so named as to indicate this relationship. Thus the five sulfo-salts whose formulas above are called ammonium sulfarsenite, sulfantimonite, sulfarsenate, are given sulfantimonate, and sulfostannate.

2. The ammonium monosulfide reagent is a solution of  $(\text{NH}_4)_2\text{S}$  and of the products of its hydrolysis,  $\text{NH}_4\text{SH}$ ,  $\text{NH}_4\text{OH}$ , and a little  $\text{H}_2\text{S}$ . The polysulfide contains in addition various polysulfides of the forms  $(\text{NH}_4)_2\text{S}_{2-5}$  and  $(\text{NH}_4)\text{HS}_{2-5}$  in unknown proportions.

3. When the polysulfide has to be employed, a small volume (5–10 cc.) is used at first, so that upon acidifying it (in P. 41) only a small quantity of sulfur will separate, thus making it possible to determine the presence or absence of tin-group sulfides.

4. In order that the separation of the copper and tin groups by ammonium sulfide may be as complete as possible, it is necessary to employ a concentrated reagent highly charged with hydrogen sulfide, and containing, in the case of the polysulfide, an appropriate excess of sulfur. Suitable reagents are prepared by completely saturating a measured volume of  $\text{NH}_4\text{OH}$  (s.g., 0.90) with  $\text{H}_2\text{S}$  in the cold, adding a fresh portion of  $\text{NH}_4\text{OH}$  (s.g., 0.90) equal to two-thirds of the original volume, and diluting a measured volume of the mixture with an equal volume of water. From this solution, which constitutes "ammonium monosulfide," the "ammonium polysulfide" is prepared by dissolving in 1 liter of it 25 grams of sulfur. These reagents, especially the monosulfide, should be kept as far as possible out of contact with the air, which is conveniently done by storing them in small, completely filled, glass-stoppered bottles; for the oxygen of the air destroys the sulfide with liberation of sulfur, which at first combines with the still unchanged sulfide, but later precipitates when the oxidation becomes more complete.

5. In separating the copper-group from the tin-group (colorless) ammonium monosulfide is used rather than (yellow) polysulfide whenever the  $\text{H}_2\text{S}$  precipitate must contain any tin and most of any antimony present in the state of the higher sulfide ( $\text{SnS}_2$  or  $\text{Sb}_2\text{S}_5$ ). This is the case when hot concentrated nitric acid was used originally in dissolving the substance, but may not be so when water or dilute  $\text{HNO}_3$  was used; hence the directions as to the choice between the two solvents. The polysulfide has the disadvantage that it dissolves a not inconsiderable quantity of  $\text{CuS}$  and  $\text{HgS}$ , thus making the tests for copper and mercury less delicate, and making it more difficult to determine from the color of the  $\text{HCl}$  precipitate obtained from the ammonium sulfide solution in P. 41 whether or not elements of the tin-group are present. The polysulfide must, nevertheless, be used if tin may be present as  $\text{SnS}$ , or much antimony as  $\text{Sb}_2\text{S}_3$ ; for in the monosulfide  $\text{SnS}$  is almost insoluble, and  $\text{Sb}_2\text{S}_3$  is only moderately soluble.

6. More specifically, the behavior of the various sulfides, when warmed with 10 cc. of these reagents, is as follows: Of the sulfides of the copper-group none dissolves to a significant extent in ammonium monosulfide. 5–10 mg.  $\text{CuS}$  and 0.5–1.0 mg.  $\text{HgS}$  may, however, dissolve in the polysulfide when the substance contains a large quantity of these elements. Yet when only 2 mg. are present, either of these elements can be detected in the analysis of the copper-group, even when the polysulfide is used, provided only one treatment with it has been made. Of the sulfides of the tin-group, 500 mg. of  $\text{As}$  as  $\text{As}_2\text{S}_3$  or  $\text{As}_2\text{S}_5$ ,

of Sb as  $Sb_2S_3$ , or of Sn as  $SnS_2$  dissolves in either the monosulfide or polysulfide, and 500 mg. of Sn as  $SnS$  or of Sb as  $Sb_2S_3$  dissolve in the polysulfide. Scarcely any  $SnS$  and only 50-100 mg. Sb as  $Sb_2S_3$  dissolve in the monosulfide.

7. Even when a quantity of only 1 or 2 mg. of arsenic or antimony is present with a large quantity (even 500 mg.) of an element of the copper group, enough is extracted by either the monosulfide or polysulfide to be detected in the subsequent tests. With tin, however, the separation is imperfect; for, when a large quantity of elements of the copper-group and only 3-5 mg. of tin are present, the whole of this may remain undissolved; indeed, when much cadmium is present and the tin is in the stannous state, as much as 15 mg. of the latter may be wholly left in the residue, even when the polysulfide is used. On this account it is necessary to test for tin in the course of the analysis of the copper group.

8. Some sulfides, especially  $CdS$ , upon washing pass through the filter in the colloidal condition; the addition of a salt, such as  $NH_4NO_3$ , prevents this by coagulating the colloidal particles.

## ANALYSIS OF THE COPPER-GROUP.

TABTE IV.—ANALYSIS OF THE COPPER-GROUP.

RESIDUE FROM AMMONIUM SULFIDE TREATMENT:  $\text{HgS}$ ,  $\text{PbS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{CuS}$ ,  $\text{CdS}$ .  
*Boil with  $\text{HNO}_3$  (P. 23).*

Residue: $\text{HgS}$ . Add $\text{Br}_2$ solution (P. 24).		Solution: $\text{Pb}$ , $\text{Bi}$ , $\text{Cu}$ , $\text{Cd}$ as nitrates. Add $\text{H}_2\text{SO}_4$ , evaporate, add water (P. 25).			
Residue: Sulfur.	Solution: $\text{HgBr}_2$ . Add $\text{SnCl}_2$ .	Precipitate: $\text{PbSO}_4$ . <i>Dissolve in <math>\text{NH}_4\text{Ac}</math>, add <math>\text{K}_2\text{CrO}_4</math> (P. 26).</i>  Yellow precipitate: $\text{PbCrO}_4$ .	Filtrate. Add $\text{NH}_4\text{OH}$ (P. 27).		
	White or gray precipitate: $\text{Hg}_2\text{Cl}_2$ or $\text{Hg}$ .		Precipitate: $\text{Bi}(\text{OH})_3$ . <i>Dissolve in <math>\text{HCl}</math>, evaporate, add to water (P. 28).</i>	Filtrate: $\text{Cu}(\text{NH}_3)_4\text{SO}_4$ , $\text{Cd}(\text{NH}_3)_4\text{SO}_4$ .	
			White precip- itate: $\text{BiOCl}$ . Add $\text{Na}_2\text{SnO}_2$ .	To a small part add $\text{HAc}$ and $\text{K}_4\text{Fe}(\text{CN})_6$ (P. 29).	To the remainder add $\text{KCN}$ and $\text{H}_2\text{S}$ (P. 30).
			Black residue: $\text{Bi}$ .	Red precipitate: $\text{Cu}_2\text{Fe}(\text{CN})_6$ . White precipitate: $\text{Cd}_2\text{Fe}(\text{CN})_6$ .	Yellow precipitate: $\text{CdS}$ .

**Procedure 23.**—*Treatment of the Sulfides with Nitric Acid.*—To the residue from the ammonium sulfide treatment (P. 22) in a casserole add 10–20 cc. of a mixture of one volume  $\text{HNO}_3$  and two volumes water, heat to boiling, and boil gently for a minute or two. (Black residue, possible presence of MERCURY.) Filter and wash. (Residue, P. 24; solution, P. 25.)

*Notes.*—1. Boiling  $\text{HNO}_3$  of this concentration dissolves the sulfides of lead, bismuth, copper, and cadmium almost immediately, and is therefore preferable to a more dilute acid, with which the reaction would require for its completion several minutes' boiling. Scarcely any  $\text{HgS}$  is dissolved by the above treatment, unless the boiling is long continued.

2. Moderately concentrated  $\text{HNO}_3$  dissolves sulfides much more rapidly than  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  of the same concentration; for with the latter acids the sulfide-ion is removed from the solution only by combination with the hydrogen-ion and by the volatilization of the  $\text{H}_2\text{S}$  formed thereby, while with  $\text{HNO}_3$  the sulfide-ion (or the  $\text{H}_2\text{S}$  in equilibrium with it) may also be destroyed by oxidation to ordinary sulfur. The oxidizing effect of  $\text{HNO}_3$  is, however, small, unless it is hot and moderately concentrated.

3. That  $\text{HgS}$ , unlike the other sulfides, does not dissolve in the dilute  $\text{HNO}_3$  is doubtless due to the much smaller concentration of its ions in its saturated solution and to the fact that at this small concentration sulfide-ion (or the  $\text{H}_2\text{S}$  in equilibrium with it at a correspondingly small concentration) is oxidized only very slowly by the dilute  $\text{HNO}_3$ .  $\text{HgS}$  is, however, readily dissolved by more vigorous oxidizing agents, such as *aqua regia* or bromin solution, since they react rapidly with sulfide-ion (or with  $\text{H}_2\text{S}$ ) even when its concentration is very small.

4. If more concentrated  $\text{HNO}_3$  be used, or if the acid become concentrated by long boiling, the black  $\text{HgS}$  is dissolved in part, and the remainder is converted into a heavy, white, difficultly soluble compound ( $\text{Hg}(\text{NO}_3)_2 \cdot 2\text{HgS}$ ).

5. When much lead, copper, or bismuth is present the sulfur formed will generally enclose enough of the undissolved sulfide to give it a black color. A black residue is therefore not necessarily  $\text{HgS}$ , but must be further tested for mercury as described in P. 24.

6. Some sulfur is always oxidized to  $\text{H}_2\text{SO}_4$  by the boiling  $\text{HNO}_3$ ; but, even in the presence of much lead,  $\text{PbSO}_4$  is not precipitated, owing to its moderate solubility in  $\text{HNO}_3$ .

7. Any  $\text{SnS}$  or  $\text{SnS}_2$  not extracted by the ammonium sulfide treatment will be converted by the  $\text{HNO}_3$  into metastannic acid ( $\text{H}_2\text{SnO}_3$ ), most of which remains undissolved. Therefore, even a light-colored residue must be carefully collected if tin is to be tested for in this group.

**Procedure 24.—Confirmatory Test for Mercury.**—Transfer the residue undissolved by  $\text{HNO}_3$  (P. 23), with the filter if necessary, to a casserole, add 10–40 cc. saturated  $\text{Br}_2$  solution, cover the dish, and warm slightly for 5–10 minutes, with frequent stirring. Boil the mixture until the bromin is expelled, and filter. (Residue, see Note 3.) Cool the solution, and add to it a few drops of  $\text{HCl}$  and one drop of  $\text{SnCl}_2$  solution; then add 3–5 cc.  $\text{SnCl}_2$  solution. (White precipitate turning gray, or gray precipitate, presence of MERCURY.) (Residue and solution, reject.)

*Notes.*—1. In the final test for mercury  $\text{HCl}$  is added to prevent the precipitation of a basic tin salt when the  $\text{SnCl}_2$  reagent is diluted, and to cause the formation at first of white  $\text{Hg}_2\text{Br}_2$  or  $\text{Hg}_2\text{Cl}_2$ . For the latter reason, also, a single drop of  $\text{SnCl}_2$  solution is first added to the cold solution. By the excess of  $\text{SnCl}_2$  the white precipitate is reduced to gray, finely divided mercury.

2. The presence of mercury at this point shows that it was originally in the mercuric state only when the substance was dissolved (in P. 2) without the use of hot or concentrated  $\text{HNO}_3$ .

3. If elements of the copper-group are present in large quantity (100–500 mg.), the residue from the  $\text{Br}_2$  treatment should be tested for tin, in order to guard against overlooking the presence of a small quantity of this element in the substance. For, as stated in P. 22, Note 3, a quantity of tin as large as 5 mg. (or even larger when stannous tin and cadmium are both present) may remain entirely in the residue undissolved by ammonium sulfide when this residue is large. To recover the tin, proceed as follows: Digest the residue from the  $\text{Br}_2$  treatment, if it is still dark-colored, with another portion of  $\text{Br}_2$

solution (to extract the rest of the mercury), filter, reject the filtrate, and warm the residue slightly with 2-5 cc. ammonium monosulfide. Filter, and unite the solution with the main ammonium sulfide solution obtained in P. 22. By this procedure 2 mg. Sn can be detected.

4. Bromin solution dissolves HgS, but leaves in the residue any metastannic acid. In case tin need not be tested for at this point, the residue may be more quickly dissolved by warming it with HCl and adding gradually a little solid KClO<sub>4</sub>. Metastannic acid, being soluble in HCl, then passes into solution with the mercuric salt, but it does not interfere with the test for mercury.

**Procedure 25.—Precipitation of Lead with Sulfuric Acid.**—To the HNO<sub>3</sub> solution (P. 23) add 2-3 cc. H<sub>2</sub>SO<sub>4</sub> (s.g., 1.84), and evaporate in a casserole until fumes of H<sub>2</sub>SO<sub>4</sub> begin to come off. Cool and pour into 10-15 cc. cold water, rinsing out the casserole with the same solution. Cool again, shake, and allow the mixture to stand 5 minutes, but not much longer. (Finely divided white precipitate, presence of LEAD (or BARIUM).) Filter and wash the precipitate with 6-normal H<sub>2</sub>SO<sub>4</sub>, and finally with a little water. (Precipitate, P. 26; filtrate, P. 27.)

*Notes.*—1. PbSO<sub>4</sub> is somewhat soluble both in water and in concentrated H<sub>2</sub>SO<sub>4</sub>, but much less so in moderately dilute H<sub>2</sub>SO<sub>4</sub>, its solubility being scarcely appreciable in mixtures containing one volume of H<sub>2</sub>SO<sub>4</sub> (s.g., 1.84) and two to six volumes of water. That the solubility in dilute H<sub>2</sub>SO<sub>4</sub> is less than that in water is due mainly to the common-ion effect. Concentrated H<sub>2</sub>SO<sub>4</sub> is, of course, an entirely different solvent. PbSO<sub>4</sub> dissolves fairly readily in dilute HNO<sub>3</sub>, owing to the tendency to form the intermediate HSO<sub>4</sub><sup>-</sup> ion; hence, to ensure complete precipitation of PbSO<sub>4</sub>, the HNO<sub>3</sub> must be removed by evaporation.

2. When much bismuth is present it ordinarily dissolves at first when the water is added to the concentrated H<sub>2</sub>SO<sub>4</sub>, provided the mixture is kept cold; but from this solution a coarsely crystalline precipitate of an oxy sulfate, such as (BiO)<sub>2</sub>SO<sub>4</sub>, separates slowly upon standing in the cold but almost immediately upon heating, and to such an extent that there may remain in solution not more than 50 mg. of bismuth. If the precipitate is of this character, free it from bismuth before applying the confirmatory test for lead by pouring repeatedly through the filter a 5-10 cc. portion of HCl and treating the solution so obtained by P. 25. The evaporation with H<sub>2</sub>SO<sub>4</sub> is necessary in order to ensure reprecipitation of the PbSO<sub>4</sub> that has been dissolved by the HCl.

**Procedure 26.—Confirmatory Test for Lead.**—Pour repeatedly through the filter containing the H<sub>2</sub>SO<sub>4</sub> precipitate (P. 25) a 10-20 cc. portion of NH<sub>4</sub>Ac solution. To the filtrate add a few drops of K<sub>2</sub>CrO<sub>4</sub> solution and 2-5 cc. HAC. (Yellow precipitate, presence of LEAD.)

*Note.*—This confirmatory test for lead should not be omitted; for the H<sub>2</sub>SO<sub>4</sub> precipitate may consist not only of PbSO<sub>4</sub> but of (BiO)<sub>2</sub>SO<sub>4</sub> or of BaSO<sub>4</sub>, which last closely resembles PbSO<sub>4</sub> in appearance. (BiO)<sub>2</sub>SO<sub>4</sub> dissolves in NH<sub>4</sub>Ac

solution and gives a yellow precipitate on adding  $K_2CrO_4$ ; but this precipitate, unlike  $PbCrO_4$ , dissolves readily in acetic acid.  $BaSO_4$  is not dissolved by  $NH_4Ac$  solution, owing to its very slight solubility in water and the fact that barium acetate, unlike lead acetate, is a largely-ionized salt. If a white residue remains, this should be tested for barium, since under some circumstances substantially the whole of this element present in the substance may be found at this point. This test may be made most simply by reserving the precipitate and adding it later to the solution from which the alkaline-earth-group is to be precipitated by  $(NH_4)_2CO_3$  (P. 81).

**Procedure 27.—Precipitation of Bismuth with Ammonium Hydroxide.**—To the  $H_2SO_4$  solution (P. 25) add  $NH_4OH$  slowly until a strong odor of it persists after shaking. (White precipitate, possible presence of BISMUTH; blue solution, presence of COPPER.) Shake to cause coagulation, filter, and wash the precipitate. (Precipitate, P. 28; filtrate, P. 29 and 30.)

*Notes.*—1. The precipitate produced by  $NH_4OH$  may consist also of  $Fe(OH)_3$ , or of other hydroxides of the iron-group, if these elements were carried down in the  $H_2S$  precipitate or were not completely removed from it by washing. The formation of a small precipitate is, therefore, not a sufficient proof of the presence of bismuth, and the confirmatory tests of P. 28 must be applied.

2.  $Cd(OH)_2$  or  $Cu(OH)_2$ , the only very slightly soluble in water, dissolves in  $NH_4OH$  owing to the combination of the  $Cd^{++}$  or  $Cu^{++}$  ion present in the saturated solutions with  $NH_3$ , forming the complex cation  $Cd(NH_3)_4^{++}$  or  $Cu(NH_3)_4^{++}$ . These complex cations have an extremely small ionization tendency; thus in a normal  $NH_4OH$  solution the ratio of the concentration of the complex cadmium ion to the simple cadmium ion is about  $10^7$ . The solubility of these hydroxides in  $NH_4OH$  is greatly increased by the presence of ammonium salts, since these salts, owing to the common-ion effect, greatly reduce the ionization of the  $NH_4OH$ , and therefore the  $OH^-$  concentration in the solution, thus enabling the  $Cd^{++}$  or  $Cu^{++}$  concentration, and therefore also the corresponding complex ion concentration, to attain a much larger value than in the saturated solutions of  $Cd(OH)_2$  or  $Cu(OH)_2$  in  $NH_4OH$  alone. It will be noticed that four distinct equilibria are involved—that between solid  $Cd(OH)_2$  or  $Cu(OH)_2$  and its ions; that between  $Cd^{++}$  or  $Cu^{++}$ ,  $NH_3$  and  $Cd(NH_3)_2^{++}$  or  $Cu(NH_3)_2^{++}$ ; that between  $NH_4OH$ ,  $NH_3$ , and  $H_2O$ ; and that between  $NH_4OH$ ,  $NH_4^+$ , and  $OH^-$ . It may be further mentioned that, since in any dilute solution the concentration of the water is substantially constant, the concentration of any hydrate (like  $NH_4OH$ ) is proportional to that of the anhydrous substance ( $NH_3$ ).

**Procedure 28.—Confirmatory Tests for Bismuth.**—Dissolve the  $NH_4OH$  precipitate (P. 27) by pouring a little  $HCl$  through the filter, evaporate off the acid almost completely, leaving the residue only barely moist with it, add 1–2 cc. water, pour the solution into a flask containing 100 cc. water heated to  $50-70^\circ$ , and allow the mixture to stand 2 or 3 minutes. (White precipitate, presence of



**BISMUTH.)** Filter the liquid (even if it looks clear), wash the filter with a little water, and pour through it a freshly prepared solution of sodium stannite. (Black residue, presence of BISMUTH.)

*Notes.*—1. The white precipitate of  $\text{BiOCl}$  formed in the first confirmatory test for bismuth is produced by the hydrolysis of  $\text{BiCl}_3$ . If  $\text{HCl}$ , the other product of the hydrolysis, is present in the solution, the reaction will not be complete, and a greater or less quantity of bismuth will remain in solution. This quantity increases rapidly with the acid concentration in accordance with the law of mass-action. For this reason, if the presence of 0.5 mg. of bismuth in the precipitate is to be detected, the  $\text{HCl}$  must be removed by evaporation so completely that not more than 0.2 cc. remain, and the solution must be added to a large volume of water. Warm water is used, because the precipitation of  $\text{BiOCl}$  takes place more rapidly at the higher temperature. Antimony under these conditions gives a similar precipitate, but it can not be present in the  $\text{HNO}_3$  solution of the sulfides in quantity sufficient to give a precipitate with  $\text{NH}_4\text{OH}$ .

2. The solution of sodium stannite ( $\text{Na}_2\text{SnO}_2$ ) is prepared when needed by adding  $\text{NaOH}$  solution to  $\text{SnCl}_2$  solution until the  $\text{Sn(OH)}_2$  first formed is dissolved. The solution must be freshly prepared, because it decomposes spontaneously into sodium stannate ( $\text{Na}_2\text{SnO}_3$ ) and metallic tin, and because it oxidizes in contact with air to sodium stannate.  $\text{SnO}_2\text{H}_2$  is an example of a so-called amphoteric substance—one which acts either as a base or an acid as is shown by its solubility in both acids and alkalis.

3. The final test with sodium stannite depends on the reduction of  $\text{BiOCl}$  to black metallic bismuth. The test is an extremely delicate one, and by it may be detected a quantity of bismuth so small as to produce only a scarcely visible turbidity of  $\text{BiOCl}$ ; for, when the precipitate in such a solution is collected on a filter and treated with stannite, the black color of the bismuth is very apparent. Antimony oxychloride, even if present, would not be blackened by the stannite. The  $\text{NH}_4\text{OH}$  precipitate itself might be directly tested with this reagent; for the other reducible substances, like  $\text{Fe(OH)}_3$ ,  $\text{Pb(OH)}_2$ , or  $\text{Cu(OH)}_2$ , that might possibly be present in that precipitate are not reduced by short contact with stannite solution in the cold. It is, however, often desirable to get the double indication of the presence of bismuth, as furnished by the precipitation of the oxychloride by water and by its blackening with the sodium stannite.

**Procedure 29.—Confirmatory Test for Copper.**—Acidify one-fourth of the  $\text{NH}_4\text{OH}$  solution (P. 27) with  $\text{HAc}$ , add one drop  $\text{K}_4\text{Fe(CN)}_6$  solution, and allow the mixture to stand for several minutes. (Red precipitate, presence of COPPER.) Then add 1–2 cc. more  $\text{K}_4\text{Fe(CN)}_6$  solution. If it is uncertain whether there is a precipitate, pour the solution through a filter and wash with a little water. (Pink color on the filter, presence of COPPER.)

*Notes.*—1. The confirmatory test for copper is more delicate than the formation of a blue color with  $\text{NH}_4\text{OH}$  (P. 27). It should, therefore, be tried even when the  $\text{NH}_4\text{OH}$  solution is colorless. Cadmium is also precipitated

and does not prevent the pink precipitate, provided only a small copper salt, owing to its smaller

solubility with excess of  $\text{NH}_4\text{OH}$ ; but no precipitate, with  $\text{K}_4\text{Fe}(\text{CN})_6$ .

*n.*—Treat the remainder with  $\text{KCN}$  solution (see Note 1), which is colorless, but enough to react for about half a minute. (See also section of CADMIUM.)

and that it is extremely poisonous. Do not breathe its fumes, especially

if the salt is reduced from the cupric to the cuprous state by excess of  $\text{KCN}$  to form the complex cuprous cyanide. This result is due to the fact that cuprous cyanide spontaneously decomposes into cuprous cyanide and cyanogen. The reaction takes place completely when  $\text{CuCN}$  by combination with the excess of cyanogen is not evolved as a gas, but as  $\text{Cu}_2\text{O}$  and cyanide and other more complex compounds.  $\text{Cu}_2\text{S}$  nor  $\text{CuS}$  is precipitated from the solution, but neither the  $\text{Cu}^{++}$  nor  $\text{Cu}^+$  of the product  $(\text{Cu}^{++}) \times (\text{S}^-)$  or  $(\text{Cu}^+) \times (\text{S}^-)$  in solutions saturated with  $\text{CuS}$  or  $\text{Cu}_2\text{S}$ . This is due to the very slight ionization of the complex anion, as it has been estimated that in a solution of the complex anion to

be converted by  $\text{KCN}$  into a complex cadmicyanide, since its complex anion is more stable than the cation  $\text{Cd}(\text{NH}_3)_4^{++}$ ; the concentration of the complex anion is about  $10^{17}$ . Yet this complex anion is the solution to become super-saturated.

It may be due to  $\text{HgS}$  or  $\text{PbS}$  may be precipitated with  $\text{H}_2\text{S}$ ; but, provided it is not in sufficient quantity to prevent the formation of a black precipitate being seen. In case a black precipitate may be treated, in order to obtain a positive conclusion as to the presence of cadmium, the precipitate gently for about 5 cc. of a mixture of one volume of  $\text{H}_2\text{S}$  into it for 5-10 minutes. A black precipitate is obtained, if cadmium is present.

## REPRECIPITATION OF THE TIN-GROUP.

**Procedure 41.**—*Reprecipitation of the Tin-Group.*—Dilute in a small flask the first portion of the ammonium sulfide solution (P. 22) with about 20 cc. water, make it distinctly acid with HCl, and warm it slightly for 5 minutes with frequent shaking to coagulate the precipitate. (Fine, not flocculent, white or pale yellow precipitate, absence of TIN-GROUP; deep yellow or orange, flocculent precipitate, presence of TIN-GROUP.) [Treat the second portion of the ammonium sulfide solution (P. 22) in the same way, and unite the precipitate, if considerable in amount, with the first one.] Filter out and wash the precipitate, using suction, finally sucking it as dry as possible. (Precipitate, P. 42; filtrates, reject.)

*Notes.*—1. In cases where the filtration is slow, where the precipitate must be washed with very little water, or where (as in this case) it must be freed as far as possible from water, it is advisable to filter with the aid of suction. This operation is carried out by reinforcing the ordinary filter with a small hardened filter placed below it in the funnel, by inserting the funnel in a rubber stopper in the neck of a filter-bottle, and connecting the side arm of the filter-bottle to a suction-pump by means of a rubber tube carrying a screw-clamp. The suction should be applied very gradually so as to avoid breaking the filter. The filtrate should be poured out of the filter-bottle before beginning to wash the precipitate.

2. When the HCl is added to the solution of the sulfosalts, the corresponding sulfoacids which are liberated decompose immediately into  $H_2S$  and the solid sulfides. These are now necessarily in the higher state of oxidation, since the lower sulfides, if originally present, have been oxidized by the polysulfide. The fact that the sulfoacids decompose while the sulfosalts are stable is a consequence of the mass-action-law. Thus, since the complex anions dissociate according to the equations,



this law evidently requires that the anion decompose to a greater extent into the unionized sulfides ( $SnS_2$ , etc.) the smaller the concentration of the  $S^-$  ion in the solution. Now in the solution of the largely ionized  $(NH_4)_2S$  there is a fairly large concentration of  $S^-$  ion; but when the solution is made acid with HCl, the  $S^-$  ion is, for the most part, converted by the relatively large concentration of the  $H^+$  ion into the slightly ionized substances  $HS^-$  and  $H_2S$ . Consequently the concentration of the unionized sulfides becomes great enough to supersaturate the solution, and the solid sulfide separates out.

3. Much time is ordinarily saved by determining at this point whether or not any element of the tin-group is present. When ammonium monosulfide has been used, there is usually no difficulty in drawing a definite conclusion in regard to this from the size and appearance of the HCl precipitate; for in the absence of the tin-group only a very small, nearly white precipitate of finely divided sulfur separates. When, however, ammonium polysulfide has been used, it may not be possible to decide as to the presence or absence of a small quantity (1-5 mg.) of arsenic, antimony, or tin; for not only is a fairly large precipitate of sulfur then obtained, but it may be darkened in color by

the presence of  $\text{CuS}$  or  $\text{HgS}$ . Yet, when the precipitate is nearly white and finely divided or granular, the conclusion can be drawn at once that no element of the tin-group is present in quantity as large as 1 mg.; and when it has a pronounced yellow color (indicating arsenic or tin) or an orange-red color (indicating antimony) the conclusion can be drawn that one of these elements is present. In this connection it may be mentioned that a mixture of  $\text{SnS}_2$  and  $\text{Sb}_2\text{S}_5$  does not always have a color intermediate between those just mentioned, but may be brown or dark gray.

4. When, however, the  $\text{HCl}$  precipitate from a polysulfide solution is fairly small and is dark brown (indicating copper) or dark gray or black (indicating mercury) or of unpronounced yellow or orange color, so as to make any conclusion as to the tin-group doubtful, the precipitate is best treated as follows: Heat it with 15–20 cc.  $\text{NH}_4\text{OH}$  almost to boiling for 5 minutes and filter; test the precipitate for copper by P. 23, 27, and 29 if it has not already been found present; add to the filtrate a few drops of ammonium monosulfide, filter out any precipitate, heat the filtrate to boiling, make it acid with  $\text{HCl}$ , shake, filter out the precipitate, and treat it by P. 42 as usual. The character of the  $\text{HCl}$  precipitate now obtained will clearly indicate the presence or absence of the tin-group; for by the treatment with  $\text{NH}_4\text{OH}$  the excess of sulfur originally present and any  $\text{CuS}$  is left undissolved, and by the  $(\text{NH}_4)_2\text{S}$  added to the solution any mercury present is precipitated, so that the  $\text{HCl}$  precipitate can contain only sulfides of the tin-group and a very little sulfur.  $\text{As}_2\text{S}_5$ ,  $\text{Sb}_2\text{S}_5$ , and  $\text{SnS}_2$  all dissolve in  $\text{NH}_4\text{OH}$  (tho in the cases of  $\text{Sb}_2\text{S}_5$  and  $\text{SnS}_2$  less abundantly than in ammonium sulfide), owing to the formation of a mixture of salts of partially sulfurated acids, such as  $\text{H}_3\text{AsO}_3\text{S}$  and  $\text{H}_3\text{AsO}_2\text{S}_2$ . The addition of  $(\text{NH}_4)_2\text{S}$  to the  $\text{NH}_4\text{OH}$  solution and the heating serve to convert these into the fully sulfurated acids, such as  $\text{H}_3\text{AsS}_4$ ; from which  $\text{HCl}$  will then precipitate the simple sulfides much more completely.—The incidental removal of the small amounts of  $\text{CuS}$  and  $\text{HgS}$  by the  $\text{NH}_4\text{OH}$  treatment is not necessary so far as the analysis of the tin-group is concerned, since their presence does not interfere with the detection of even 1 mg. of arsenic, antimony, or tin; but it does enable 1 or 2 mg. of copper to be detected which might otherwise be lost.

## ANALYSIS OF THE TIN-GROUP.

TABLE V.—ANALYSIS OF THE TIN-GROUP.

PRECIPITATE FROM AMMONIUM SULFIDE SOLUTION: $\text{As}_2\text{S}_5$ , $\text{Sb}_2\text{S}_5$ , $\text{SnS}_2$ . Heat with 10 cc. $\text{HCl}$ (s.g., 1.20) (P. 42).		
Solution: $\text{SbCl}_3$ , $\text{SnCl}_4$ . Dilute to 50 cc., heat, and pass in $\text{H}_2\text{S}$ (P. 45).		Residue: $\text{As}_2\text{S}_5$ . Dissolve in $\text{HCl}$ and $\text{KClO}_3$ (P. 43).
Orange precipitate: $\text{Sb}_2\text{S}_3$ . Dissolve in $\text{HCl}$ , add $\text{Sn}$ and $\text{Pt}$ (P. 46).	Solution: $\text{SnCl}_4$ . Cool, dilute, pass in $\text{H}_2\text{S}$ (P. 47).	Solution: $\text{H}_3\text{AsO}_4$ . Add $\text{NH}_4\text{OH}$ , $\text{NH}_4\text{Cl}$ , and $\text{MgCl}_2$ (P. 44).
Black deposit: $\text{Sb}$ . Treat with $\text{NaOCl}$ .	Yellow precipitate: $\text{SnS}_2$ . Dissolve in $\text{HCl}$ , add $\text{Zn}$ (P. 47).	White precipitate: $\text{MgNH}_4\text{AsO}_4$ . Dissolve in $\text{HCl}$ , add $\text{H}_2\text{S}$ (P. 44).
Black deposit: $\text{Sb}$ .	Gray deposit: $\text{Sn}$ . Dissolve in $\text{HCl}$ , add $\text{HgCl}_2$ (P. 47).	Yellow precipitate: $\text{As}_2\text{S}_5$ , $\text{As}_2\text{S}_3$ , and $\text{S}$ .
	White precipitate: $\text{Hg}_2\text{Cl}_2$ .	

**Procedure 42.**—*Treatment of the Sulfides with Strong Hydrochloric Acid.*—Transfer the precipitated sulfides dried by suction (P. 41) to a wide test-tube, add from a small graduate exactly 10 cc.  $\text{HCl}$  (s.g., 1.20), and heat nearly but not quite to boiling (preferably by immersing the test-tube in boiling water or in a steam bath) for about 10 minutes with frequent stirring. Add 5 cc. water from a graduate containing 40 cc. water, filter, wash once with about 5 cc. water from the graduate, collecting this wash-water with the filtrate; remove the filtrate, and add to it the water remaining in the graduate; wash the residue with  $\text{HCl}$  (s.g., 1.10). (Residue, P. 43; filtrate, P. 45.)

*Notes.*—1. If a much weaker  $\text{HCl}$  solution than the acid of specific gravity 1.20 is used, or if the acid becomes diluted by an unnecessary quantity of water left in the precipitate, much  $\text{Sb}_2\text{S}_5$  will be left undissolved. Even with the strong acid some  $\text{Sb}_2\text{S}_5$  may remain undissolved, especially when a large quantity is present, in which case the residue if small in amount will have an orange color. This small quantity of  $\text{Sb}_2\text{S}_5$  would be only very slowly removed by further treatments with  $\text{HCl}$ ; it does not, however, interfere with the subsequent tests for arsenic. Moreover, when only a small quantity of  $\text{Sb}_2\text{S}_5$  is

originally present, a large proportion of it is extracted, so that it will not escape detection.  $\text{Sb}_2\text{S}_5$  dissolves with formation of  $\text{SbCl}_3$  and liberation of sulfur;  $\text{SnS}_2$ , with formation of  $\text{SnCl}_4$ .

2. If the solution be kept just below the boiling-point during the treatment with  $\text{HCl}$ , the amount of  $\text{As}_2\text{S}_5$  which dissolves in ten minutes is insignificant. But this is no longer true if the solution be allowed to boil; for the boiling rapidly expels from the solution the  $\text{H}_2\text{S}$  liberated from the other sulfides or by slight decomposition of the  $\text{As}_2\text{S}_5$  itself, and thus enables the decomposition of the latter to proceed further.

3.  $\text{As}_2\text{S}_3$  is more rapidly dissolved by  $\text{HCl}$  than is  $\text{As}_2\text{S}_5$ . If the former can be present in the precipitate (which can be the case only when ammonium monosulfide was used for separating the copper and tin groups), the procedure should be modified by saturating with  $\text{H}_2\text{S}$  gas the cold concentrated  $\text{HCl}$  with which the sulfides are treated, and by passing a slow current of  $\text{H}_2\text{S}$  gas through the mixture during the heating. Under these conditions scarcely any  $\text{As}_2\text{S}_3$  dissolves.

4. About 5 cc. water are added to the  $\text{HCl}$  solution to enable it to be filtered. If more is added and the  $\text{H}_2\text{S}$  has not all been expelled from the solution, a precipitate of  $\text{Sb}_2\text{S}_3$  may separate. If this happens after the filtration, it does, of course, no harm.

5. Care must be taken to follow closely the directions in regard to the quantities of  $\text{HCl}$  and water used; for the subsequent separation of antimony and tin (P. 45) depends upon a proper concentration of the acid.

6. The greater part of any  $\text{CuS}$  and  $\text{HgS}$  present will be dissolved by the  $\text{HCl}$ , and will be precipitated later with the  $\text{Sb}_2\text{S}_3$  (P. 45). A little remains with the  $\text{As}_2\text{S}_5$ , but this does not interfere with the tests for arsenic.

**Procedure 43.—Detection of Arsenic.**—Warm the residue from the  $\text{HCl}$  treatment (P. 42) with 5–10 cc. 6-normal  $\text{HCl}$ , adding solid  $\text{KClO}_3$  in small portions until the reaction is complete; filter off the sulfur, and evaporate the solution to about 2 cc. Add  $\text{NH}_4\text{OH}$  gradually until the solution after shaking smells of it; cool, filter off and reject any precipitate. Add to the filtrate in a test-tube about one-third its volume of  $\text{NH}_4\text{OH}$  (s.g., 0.90) and several drops of magnesium ammonium chloride reagent, and shake. If no precipitate appears, rub the walls of the test-tube gently with a glass rod for a minute or two. (White crystalline precipitate, presence of ARSENIC.) Collect the precipitate on a filter and wash it once with  $\text{NH}_4\text{OH}$  (s.g., 0.96). (Precipitate, P. 44; filtrate, reject.)

**Notes.**—1. The main reaction between  $\text{KClO}_3$  and concentrated  $\text{HCl}$  is the formation of  $\text{Cl}_2$ ; the yellow color results from the formation of a small proportion of chlorine dioxide,  $\text{ClO}_2$ .

2.  $\text{As}_2\text{S}_5$ , the only very slowly dissolved by  $\text{HCl}$  alone, is dissolved rapidly by it in the presence of  $\text{Cl}_2$ , because of the destruction by oxidation of the sulfide-ion and of the  $\text{H}_2\text{S}$  formed from it. The same principles are involved as in the action of  $\text{HNO}_3$  on sulfides (see P. 23, Note 2). It is dissolved with formation of  $\text{H}_3\text{AsO}_4$ ;  $\text{AsCl}_5$  has not been shown to exist. When, as here,

arsenic is present in the higher state of oxidation, solutions of it may be boiled without loss of an amount of arsenic significant in qualitative analysis.

3. A white precipitate produced on adding  $\text{NH}_4\text{OH}$  may arise from the presence of mercury. The  $\text{NH}_4\text{OH}$  solution may contain not only arsenic, but also the small quantities of copper (if ammonium polysulfide was used), antimony, and stannic tin that were not dissolved out of the sulfide precipitate by  $\text{HCl}$ .

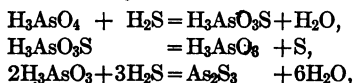
4. The test for arsenic depends on the formation of magnesium ammonium arsenate,  $\text{Mg}(\text{NH}_4)\text{AsO}_4$ . This salt is somewhat soluble even in cold water, and therefore the solution tested should be fairly concentrated. Owing to hydrolysis (into  $\text{NH}_4\text{OH}$  and  $\text{Mg}^{++}\text{HAsO}_4^-$ ), the precipitate is much more soluble in water than in a strong  $\text{NH}_4\text{OH}$  solution; hence the addition of a large quantity of the latter. Like other crystalline precipitates, it tends to form a supersaturated solution. Precipitation is promoted by agitation, by rubbing the walls of the tube with a glass rod, and by increasing the degree of supersaturation, which is done by concentrating the solution and adding  $\text{NH}_4\text{OH}$ . Provided these precautions are taken and the total volume of the final solution does not exceed 5 cc., the presence of 0.5 mg. of arsenic can be detected. Care must be taken not to scratch the glass by violent rubbing, since the powdered glass may be mistaken for the  $\text{MgNH}_4\text{AsO}_4$  precipitate.

5. The magnesium ammonium chloride reagent contains  $\text{MgCl}_2$  and  $\text{NH}_4\text{Cl}$ . The presence of the latter salt, by reducing the  $\text{OH}^-$  concentration, prevents the precipitation of  $\text{Mg}(\text{OH})_2$  by  $\text{NH}_4\text{OH}$ .

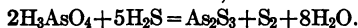
**Procedure 44.—Confirmatory Test for Arsenic.**—Dissolve the  $\text{MgCl}_2 \cdot \text{NH}_4\text{Cl}$  precipitate (P. 43) by pouring a little  $\text{HCl}$  through the filter, saturate the solution with  $\text{H}_2\text{S}$ , heat it nearly to boiling, and pass in  $\text{H}_2\text{S}$  for 5 minutes. (White precipitate turning yellow, presence of ARSENIC.) (Precipitate and solution, reject.)

*Notes.*—1. The slow formation of a pale yellow precipitate with  $\text{H}_2\text{S}$  is a characteristic test for  $\text{H}_3\text{AsO}_4$ . The precipitate is a mixture of  $\text{As}_2\text{S}_5$ ,  $\text{As}_2\text{S}_3$ , and sulfur; but the proportion of  $\text{As}_2\text{S}_5$  is comparatively small when the precipitation takes place from a hot solution.

2. A considerable amount of  $\text{H}_2\text{S}$  is absorbed by a cold  $\text{H}_3\text{AsO}_4$  solution before any precipitate appears. This is due to the conversion of a part of the  $\text{H}_3\text{AsO}_4$  into  $\text{H}_3\text{AsO}_3\text{S}$ , which then decomposes slowly, giving  $\text{H}_3\text{AsO}_3$  and sulfur. This last decomposition is accelerated by increasing the  $\text{H}^+$  concentration and by raising the temperature. The  $\text{H}_3\text{AsO}_3$  formed reacts at once with  $\text{H}_2\text{S}$ , and  $\text{As}_2\text{S}_3$  is precipitated. The reactions taking place are:

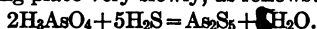


which together give the resultant reaction,



The rate of this reaction depends upon the rate of the slowest of the separate reactions—the decomposition of the  $\text{H}_3\text{AsO}_3\text{S}$ —and on the quantity of this substance which has been produced by the first reaction. This quantity seems to be determined by the equilibrium-conditions of the first reaction rather

than by its rate; for it is larger when the solution is saturated in the cold with  $\text{H}_2\text{S}$ , doubtless owing to the greater solubility of the  $\text{H}_2\text{S}$  in the cold solution. This explains why it is advantageous to saturate the solution with  $\text{H}_2\text{S}$  first in the cold. Having formed in this way as large a proportion of  $\text{H}_3\text{AsO}_3\text{S}$  as possible, the solution is then heated in order to cause decomposition of this substance according to the second reaction.— $\text{As}_2\text{S}_5$  is produced by an independent reaction, taking place very slowly, as follows:



**Procedure 45.—Separation of Antimony and Tin.**—Heat the solution of the sulfides (P. 42), which should contain 10 cc.  $\text{HCl}$  (s.g., 1.20) in a total volume of 50 cc., to about  $90^\circ$ , and pass in  $\text{H}_2\text{S}$  gas for about 5 minutes, keeping the solution at about  $90^\circ$ . If no precipitate appears, add about 5 cc. water, and again saturate with  $\text{H}_2\text{S}$  at the same temperature as before. (Orange-red precipitate, presence of ANTIMONY.) Filter while hot, add 5 cc. water, heat the filtrate nearly to boiling, again saturate it with  $\text{H}_2\text{S}$  to ensure complete precipitation of antimony, and if a further precipitate forms, collect it on a separate filter. Wash the precipitates with hot water. (Precipitate, P. 46; filtrate, P. 47.)

*Notes.*—1. By following carefully the directions given in P. 42 and in this procedure, a good separation of antimony and tin may be obtained; thus, when only 1 mg. of antimony is present it is precipitated, while even 500 mg. of (stannic) tin give no precipitate. If, however, the  $\text{HCl}$  solution be too concentrated, a small quantity of antimony will escape detection; hence the precaution of adding a little water to the solution and repeating the treatment with  $\text{H}_2\text{S}$ . If the  $\text{HCl}$  solution be too dilute, or if it be not kept hot, some  $\text{SnS}_2$  may precipitate when a large amount of tin is present. When  $\text{SnS}_2$  is mixed with a little  $\text{Sb}_2\text{S}_3$  a brown precipitate results.

2. If mercury or copper be present in the substance and ammonium polysulfide has been used,  $\text{HgS}$  or  $\text{CuS}$  may be precipitated at this point as a gray or black precipitate.

**Procedure 46.—Confirmatory Test for Antimony.**—Dissolve the  $\text{H}_2\text{S}$  precipitate (P. 45) in a little  $\text{HCl}$  (s.g., 1.20) in a small casserole, and evaporate the solution to about 1 cc. Introduce beneath the solution a piece of platinum foil and place upon it a piece of pure tin. After several minutes wash the platinum foil carefully with water and cover it with (alkaline)  $\text{NaOCl}$  solution. (Black deposit on the platinum undissolved by  $\text{NaOCl}$ , presence of ANTIMONY.) (Precipitate and solution, reject.)

*Notes.*—1. Mercury and copper, if present, will also be precipitated in the metallic condition upon the platinum, but the antimony may be easily distinguished from them by its black color. Tin is used, rather than zinc, in precipitating the antimony, since zinc would also precipitate tin from the solution.



2. The treatment with  $\text{NaOCl}$  serves to prove that the black precipitate does not consist of arsenic; for this element is readily dissolved by it, while antimony is not. Since, however, 5–10 mg. of arsenic must be present before the treatment with tin would give a deposit on the platinum, an arsenic deposit will probably never be obtained in an actual analysis.

**Procedure 47.—Detection of Tin.**—Cool the filtrate from the  $\text{H}_2\text{S}$  precipitate (P. 45), dilute with 20 cc. water, and pass in  $\text{H}_2\text{S}$  for 10 minutes. (Yellow precipitate, presence of  $\text{TIN}$ .) If there is a precipitate, evaporate the mixture without filtering to 5–10 cc., add about 1 g. of granulated zinc, and allow the action to continue for several minutes, but not until all the zinc is dissolved. (Gray, spongy precipitate, presence of  $\text{TIN}$ .) Decant the solution into a test-tube, allow the particles suspended in it to settle out, decant again, and unite the two residues. Heat the residues with 2–5 cc.  $\text{HCl}$  (s.g., 1.20) until everything (except any particles of carbon) is dissolved. Dilute the solution with one-half its volume of water, and pour it at once through a small filter into 5 cc.  $\text{HgCl}_2$  solution. (White precipitate, presence of  $\text{TIN}$ .)

*Notes.*—1. The solution is precipitated with  $\text{H}_2\text{S}$  in the cold, because a small quantity of  $\text{SnS}_2$  would not separate from a hot solution unless the acid were more diluted. The addition of much water is avoided, since it has to be evaporated off in the confirmatory test.

2. With respect to the confirmatory test the following points deserve mention. The precipitate of  $\text{SnS}_2$  is not filtered off, but is dissolved by concentrating the acid by evaporation, since it clogs the filter and tends to pass through it. The zinc must not be allowed to dissolve entirely, since the tin might then also dissolve. Care must be taken not to lose the tin in the process of decantation or by failing to dissolve it completely. Finally, since  $\text{SnCl}_2$  oxidizes rapidly in the air, the solution in  $\text{HCl}$  must be immediately added to the  $\text{HgCl}_2$  solution. If these precautions are observed, the presence of 0.5 mg.  $\text{Sn}$  in the  $\text{HCl}$  solution of the sulfides (P. 42) may be detected after some practice. The confirmatory test is, however, less delicate than the precipitation by  $\text{H}_2\text{S}$ ; but it is more characteristic, since  $\text{SbCl}_3$ , even if present, does not reduce  $\text{HgCl}_2$ .

## PRECIPITATION AND SEPARATION OF THE ALUMINUM AND IRON GROUPS.

See Table II, page 34.

**Procedure 51.**—*Precipitation of the Aluminum and Iron Groups.*—Boil the filtrate from the  $\text{H}_2\text{S}$  precipitate (P. 21) till the  $\text{H}_2\text{S}$  is expelled. Add to it 10 cc.  $\text{NH}_4\text{OH}$ , shake, and note whether there is a precipitate. Add ammonium monosulfide slowly (or, in case nickel seems to be present, pass in  $\text{H}_2\text{S}$ ) until, after shaking, the vapors in the flask blacken a piece of filter-paper moistened with  $\text{PbAc}_2$  solution. To coagulate the precipitate shake the mixture or heat it nearly to boiling. Filter, and wash the precipitate, first with water containing about 1% of the  $(\text{NH}_4)_2\text{S}$  reagent, and then with a little pure water. If the filtration is slow, keep the funnel covered with a watch-glass. To the filtrate add a few drops  $(\text{NH}_4)_2\text{S}$ , boil the mixture for a few seconds (or, in case it is dark colored, until it becomes colorless or light yellow); filter if there is a precipitate, uniting it with the preceding one. (Precipitate, P. 52; filtrate, P. 81.)

*Notes.*—1. The  $\text{H}_2\text{S}$  is boiled out and the effect of the addition of  $\text{NH}_4\text{OH}$  alone is noted because it often gives a useful indication as to what elements are present. To save time the expulsion of the  $\text{H}_2\text{S}$  may be omitted when this indication is considered unimportant. Only a slight excess of ammonium monosulfide is used, in order to prevent as far as possible dissolving the  $\text{NiS}$ . By passing  $\text{H}_2\text{S}$  into the ammoniacal solution, instead of adding  $(\text{NH}_4)_2\text{S}$ , the dissolving of  $\text{NiS}$  is entirely prevented; therefore, tho the operation takes a little longer, the use of  $\text{H}_2\text{S}$  is to be preferred when nickel is likely to be present. The mixture is shaken in order to coagulate the precipitate and make it filter more readily. Heating also promotes the coagulation of the precipitate; heat is therefore applied when the precipitate does not coagulate and settle quickly on shaking. The filtrate is boiled for a few moments to ensure the complete precipitation of  $\text{Cr}(\text{OH})_3$ , or longer to ensure that of  $\text{NiS}$ , whose presence is indicated by a brown or nearly black color of the filtrate. Finally, it is directed to wash with water containing a little  $(\text{NH}_4)_2\text{S}$  and to keep the filter covered, in order that some excess of  $(\text{NH}_4)_2\text{S}$  may always be present; for, if the  $(\text{NH}_4)_2\text{S}$  adhering to the precipitate is removed by oxidation or by volatilization (as  $\text{H}_2\text{S}$  and  $\text{NH}_3$ ), the sulfides are oxidized to soluble sulfates by the air.

2. Under the conditions of the procedure, which provides for a small excess of  $\text{NH}_4\text{OH}$  in the presence of ammonium salt, aluminum, chromium, and iron are completely precipitated.  $\text{Al}(\text{OH})_3$  is white;  $\text{Cr}(\text{OH})_3$ , grayish green. The color of the precipitated iron hydroxide varies with the state of oxidation of the iron, pure ferrous salts yielding a white precipitate, and ferric salts a reddish brown one, while mixtures of them yield green or black precipitates; in the alkaline mixture the precipitate is rapidly oxidized by the oxygen of the air and undergoes corresponding changes in color. Manganous salts are also oxidized rapidly, with the result that brown  $\text{Mn}(\text{OH})_3$  separates. Under the conditions of the procedure zinc and nickel, when present alone, are completely dissolved; the same is true of cobalt, except when it is present in large quantity; but zinc

is precipitated when chromium is also present. The ammoniacal solution of nickel is blue and that of cobalt of a reddish color. The latter darkens rapidly on exposure to the air, owing to oxidation. If a smaller excess of  $\text{NH}_4\text{OH}$  is used than is directed, some zinc hydroxide, as well as cobalt hydroxide, may remain undissolved when large amounts of these elements are present, but this has no effect on the subsequent analysis. If, on the other hand, a much larger excess of  $\text{NH}_4\text{OH}$  is employed, a few milligrams of aluminum and chromium may be dissolved, the latter giving a pink colored solution.

3. The presence of ammonium salts in the solution serves to prevent the precipitation of  $\text{Mg}(\text{OH})_2$ , and also to lessen the amount of  $\text{Al}(\text{OH})_3$  dissolved by the  $\text{NH}_4\text{OH}$ .

4. The influence of an excess of the  $\text{NH}_4\text{OH}$  and of the presence of ammonium salt on the solubilities of the various hydroxides is explained by the mass-action law and ionic theory as follows: In order that any hydroxide, say of the type  $\text{MO}_2\text{H}_2$ , may be precipitated, it is necessary that the product  $(\text{M}^{++}) \times (\text{OH}^-)^2$  of the concentrations of the ions  $\text{M}^{++}$  and  $\text{OH}^-$  in the solution in question attain the definit value which is known as the solubility-product. This value varies, of course, with the nature of the hydroxide, but for all the elements of the iron-group and for magnesium, it is so small that even in a solution containing in 50 cc. only 1 mg. of the element and a slight excess of  $\text{NH}_4\text{OH}$ , the product  $(\text{M}^{++}) \times (\text{OH}^-)^2$  exceeds it, and precipitation results. When, however, much ammonium salt is also present, this greatly reduces, in virtue of the common-ion effect, the ionization of the  $\text{NH}_4\text{OH}$  and therefore the  $\text{OH}^-$  concentration in the solution, so that now for certain elements the product  $(\text{M}^{++}) \times (\text{OH}^-)^2$  does not reach the value of the solubility-product, even when  $(\text{M}^{++})$  is moderately large (say 500 mg. in 50 cc.). This is true of magnesium and manganese; but in the cases of aluminum, chromium, and ferric iron the solubility of the hydroxides in water is so slight that even in ammonium salt solution the solubility is not appreciable.

If these were the only effects involved, the greater the excess of  $\text{NH}_4\text{OH}$  added, the less would be the solubility of any hydroxide; but other influences come into play with certain of the elements. These influences are of two kinds. The first of these is shown by zinc, nickel, and cobalt. In the case of these elements, just as with silver and copper, the excess of ammonia combines with the simple cation  $\text{M}^{++}$ , forming complex cations of the types  $\text{M}(\text{NH}_3)_2^{++}$  and  $\text{M}(\text{NH}_3)_4^{++}$ , thereby removing the simple cation from the solution and making it necessary for more of the hydroxide to dissolve in order to bring back the value of  $(\text{M}^{++}) \times (\text{OH}^-)^2$  to that of the solubility-product. In such a case the presence of ammonium salt increases the solubility still further, since it greatly decreases the value of  $(\text{OH}^-)$ , owing to the common-ion effect on the ionization of the  $\text{NH}_4\text{OH}$ . Chromium also forms similar ammonia complexes, but in much smaller proportion.

The second kind of effect is exhibited in the case of  $\text{AlO}_2\text{H}_3$ . This hydroxide is another example of an amphoteric substance; for it behaves both as a base and as an acid in consequence of its being appreciably ionized both into  $\text{OH}^-$  and  $\text{Al}^{+++}$  and into  $\text{H}^+$  and  $\text{AlO}_2\text{H}_2^-$  (or into  $\text{H}^+$ ,  $\text{AlO}_2^-$ , and  $\text{H}_2\text{O}$ ). With the  $\text{H}^+$  arising from the latter form of ionization the  $\text{OH}^-$  coming from the excess of  $\text{NH}_4\text{OH}$  combines to form  $\text{H}_2\text{O}$ , so as to satisfy the mass-action expression for the ionization of water,  $(\text{H}^+) \times (\text{OH}^-) = \text{a constant}$  (which

has the very small value  $10^{-14}$  at  $25^\circ$ ). This causes more  $\text{AlO}_3\text{H}_3$  to dissolve until the value of  $(\text{AlO}_3^-) \times (\text{H}^+)$  again attains that of the solubility-product. This shows that the quantity of aluminum dissolved increases with the  $\text{OH}^-$  concentration in the solution, and that therefore it would be much greater in a solution of a largely ionized base like  $\text{NaOH}$  than in that of a slightly ionized base like  $\text{NH}_4\text{OH}$ . It also shows that the presence of ammonium salts tends to neutralize the solvent action of an excess of  $\text{NH}_4\text{OH}$ , since they decrease the  $\text{OH}^-$  concentration in its solution.

5. It follows from the statements in the preceding notes that, if  $\text{NH}_4\text{OH}$  produces no precipitate, it proves the absence of as much as 1 mg. of aluminum and iron; also of chromium, if the mixture is heated to boiling after the addition of  $\text{NH}_4\text{OH}$ . Care must be taken not to overlook a small precipitate which might otherwise escape detection on account of its transparency. The mixture should therefore be well shaken and allowed to stand 2 or 3 minutes, in order that the precipitate may collect in flocks. This treatment also oxidizes the iron when present in small quantity, and thus enables it to be more readily detected; for its precipitation in the ferric state is more complete.

6. When phosphate is present, magnesium, calcium, strontium, barium, and manganese may be partially, or even completely, precipitated by  $\text{NH}_4\text{OH}$ . The reasons for this are as follows. The normal phosphates and the monohydrogen phosphates of these elements are difficultly soluble in water, but dissolve readily in acids, owing to the formation in solution of the much more soluble dihydrogen phosphates and of free phosphoric acid. Upon the addition of an excess of  $\text{NH}_4\text{OH}$  to such a solution these acid compounds are converted into the normal phosphates, and these are reprecipitated. It is therefore necessary, when phosphate is present, to provide for the detection of the alkaline-earth elements in the analysis of the  $\text{NH}_4\text{OH}$  precipitate. They are, however, not necessarily found in that precipitate; for, when other elements, like iron and aluminum, which form much less soluble phosphates are also present, they may combine with all the phosphate radical present, thus leaving the alkaline-earth elements in solution.

7. The presence of any other acidic constituent which forms with the alkaline-earth elements salts soluble in dilute acids but insoluble in ammonia may also cause their precipitation at this point. Fluoride is the only common inorganic constituent of this kind, and it will ordinarily have been removed in the evaporation with acids in the preparation of the solution.

8.  $(\text{NH}_4)_2\text{S}$  precipitates  $\text{ZnS}$ ,  $\text{MnS}$ ,  $\text{NiS}$ , and  $\text{CoS}$ , and converts  $\text{Fe}(\text{OH})_2$  into  $\text{FeS}$ , and  $\text{Fe}(\text{OH})_3$  into  $\text{Fe}_2\text{S}_3$ . The hydroxides of aluminum and chromium are not affected by the  $(\text{NH}_4)_2\text{S}$ .

9. The sulfides of iron, nickel, and cobalt are black;  $\text{ZnS}$  is white; and  $\text{MnS}$  is flesh-colored, but turns brown on standing in the air, owing to oxidation to hydrated  $\text{Mn}_2\text{O}_3$ .

10. When nickel is present alone or when it forms a large proportion of the  $(\text{NH}_4)_2\text{S}$  precipitate, several milligrams of it usually pass into the filtrate, giving it a brown or black color; and some  $\text{NiS}$  also passes through the filter with the wash-water. In this case it is useless to try to remove the  $\text{NiS}$  by filtering again, but it can be coagulated by boiling for several minutes. The brown solution is formed only in the presence of ammonium polysulfide. Its formation can, as stated above, be avoided altogether by passing  $\text{H}_2\text{S}$  into the

$\text{NH}_4\text{OH}$  solution, instead of adding the ammonium monosulfide reagent, which after exposure to the air always contains some polysulfide. The nature of the brown solution is not known.

**Procedure 52.**—*Separation of the Aluminum-Group from the Iron-Group.*—Transfer the  $(\text{NH}_4)_2\text{S}$  precipitate (P. 51), with the filter if necessary, to a casserole; add 5–20 cc.  $\text{HCl}$ , stir for a minute or two in the cold, and then boil the mixture for 2 or 3 minutes; if a black residue still remains, add a few drops  $\text{HNO}_3$  (s.g., 1.42) and boil again. Dilute with a little water, filter off the sulfur residue, and evaporate the filtrate to a small volume to remove the excess of acid. 1–3 cc  
 $\text{KClO}_3$

Dilute the solution to 10 or 20 cc., and make it alkaline with  $\text{NaOH}$  solution, avoiding a great excess, and adding 10–20 cc. more water if so large a precipitate separates that the mixture becomes thick with it. Cool by placing the casserole in cold water and add 0.5–3 g. solid  $\text{Na}_2\text{O}_2$  in small portions with constant stirring. (Then add 10 cc.  $\text{Na}_2\text{CO}_3$  solution) boil for 2 or 3 minutes to decompose the excess of  $\text{Na}_2\text{O}_2$ , cool, dilute with an equal volume of water, filter with the help of suction, and wash with hot water. (Precipitate, P. 61; filtrate, P. 53.) 1–3 cc  
*hard filter*

**Notes.**—1. All the hydroxides and all the sulfides, except  $\text{NiS}$  and  $\text{CoS}$ , usually dissolve readily in cold  $\text{HCl}$ . If, therefore, there is considerable black residue after adding the  $\text{HCl}$ , it shows the presence of nickel or cobalt; a very small black residue may, however, be due to  $\text{FeS}$  enclosed within sulfur. The fact that there is no such dark-colored residue does not, however, prove that nickel and cobalt are entirely absent; for a considerable quantity of them (even 5 mg.) may dissolve completely in the  $\text{HCl}$  when large quantities of other elements, especially iron, are also present.

2. The  $(\text{NH}_4)_2\text{S}$  precipitate is first treated with  $\text{HCl}$ , partly in order to furnish the indication just referred to of the presence of nickel or cobalt, but also because much more free sulfur and sulfate would be formed by oxidation if  $\text{HNO}_3$  or *aqua regia* were used at the start. (The presence of much sulfate in the solution interferes with the subsequent test for chromate.) If  $\text{NiS}$  or  $\text{CoS}$  is present in the residue,  $\text{HNO}_3$  must, however, be subsequently added, to ensure the solution of these sulfides.

3. By  $\text{NaOH}$ , iron, manganese, nickel, and cobalt are completely precipitated and do not dissolve in moderate excess; while aluminum, chromium, and zinc remain in solution or dissolve when a sufficient excess is added. The solubility of the last three elements is due to the fact that their hydroxides are amphoteric substances which form with the  $\text{NaOH}$  soluble aluminate ( $\text{NaAlO}_2$ ), chromite ( $\text{NaCrO}_2$ ), and zincate ( $\text{Na}_2\text{ZnO}_2$ ), respectively. When zinc and chromium are simultaneously present they are precipitated in the form of a double compound ( $\text{ZnCr}_2\text{O}_4$ ). Chromium would also be completely precipitated, owing to hydrolysis of the chromite and the formation of a less soluble solid hydroxide, if the  $\text{NaOH}$  solution were boiled before adding  $\text{Na}_2\text{O}_2$ .  $\text{Mn}(\text{OH})_2$  is white, but rapidly turns brown, owing to oxidation to  $\text{Mn}(\text{OH})_3$ ;

$\text{Ni}(\text{OH})_2$  is light green;  $\text{Co}(\text{OH})_2$  is pink, but from cold cobalt-salt solutions a blue basic salt is first precipitated. If a large excess of  $\text{NaOH}$  be added, a little  $\text{Co}(\text{OH})_2$  dissolves, yielding a blue solution, doubtless forming a salt such as  $\text{Na}_2\text{CoO}_2$ . This is to be avoided, since then the cobalt will not be completely oxidized and precipitated upon the subsequent addition of  $\text{Na}_2\text{O}_2$ .

4. By the addition of  $\text{Na}_2\text{O}_2$ ,  $\text{Fe}(\text{OH})_2$  is changed to dark red  $\text{Fe}(\text{OH})_3$ ,  $\text{Mn}(\text{OH})_2$  to brown hydrated  $\text{MnO}_2$ ,  $\text{Co}(\text{OH})_2$  to black  $\text{Co}(\text{OH})_3$ , and  $\text{Ni}(\text{OH})_2$  partially to black  $\text{Ni}(\text{OH})_3$ , all of which are insoluble in excess of cold  $\text{NaOH}$  and remain in the precipitate. Chromium, which after the addition of cold  $\text{NaOH}$  is present as soluble sodium chromite, is converted by  $\text{Na}_2\text{O}_2$  into chromate ( $\text{Na}_2\text{CrO}_4$ ). This remains in solution together with the zinc, which is still present as zincate.

5. Even a cold solution of  $\text{Na}_2\text{O}_2$  decomposes rapidly with evolution of oxygen, and this decomposition takes place with explosiv violence when the solution is hot. The peroxide is therefore added in small portions to the cold solution. A steady evolution of gas continuing after the mixture has been well stirred is an indication that sufficient peroxide has been added. The solution is diluted before filtering in order to avoid the disintegration of the filter-paper. It is also often advantageous to support the filter by folding it together with a small, hardened filter.

6. This separation with  $\text{NaOH}$ ,  $\text{Na}_2\text{O}_2$ , and  $\text{Na}_2\text{CO}_3$  is a very satisfactory one, except in the case of zinc. This element, when present in small quantities, is completely carried down in the precipitate when much iron, nickel, or cobalt, or especially manganese, is present. Provision for the detection of zinc in the precipitate must therefore be made.

7. The  $\text{Na}_2\text{CO}_3$  is added to ensure the complete precipitation of magnesium, calcium, strontium, and barium, whose hydroxides, especially that of barium, are somewhat soluble even in the presence of  $\text{NaOH}$ .  $\text{ZnCO}_3$ , tho insoluble in a dilute solution of  $\text{Na}_2\text{CO}_3$  alone, dissolves when much  $\text{NaOH}$  is present, owing to nearly complete conversion of the zinc-ion into zincate-ion ( $\text{ZnO}_2^-$ ). The  $\text{Na}_2\text{CO}_3$  also serves to decompose the chromates of the alkaline-earth elements; if it is not added, chromium may remain in the precipitate and escape detection. It is unnecessary to add the  $\text{Na}_2\text{CO}_3$  when the alkaline-earth elements are known to be absent.

8. Phosphate, if present, divides itself in this procedure between the precipitate and solution in a proportion which depends on the nature and quantities of the basic elements present. (See P. 51, Note 6.) Its presence does not cause any of the elements to precipitate which would not otherwise do so, in spite of the slight solubility of aluminum and zinc phosphates. This is due to the fact that the cations of these elements ( $\text{Al}^{+++}$ ,  $\text{Zn}^{++}$ ) are present in the  $\text{NaOH}$  solution only at an extremely small concentration, owing to their conversion by the  $\text{OH}^-$  into anions ( $\text{AlO}_2^-$ ,  $\text{ZnO}_2^-$ ).

9. If  $\text{Na}_2\text{O}_2$  is not available, sodium hypobromite,  $\text{NaBrO}$  (prepared by mixing  $\text{NaOH}$  and bromin, as described in P. 70, Note 3), may be used as the oxidizing agent; but it is not quite so satisfactory as  $\text{Na}_2\text{O}_2$ , for it does not oxidize  $\text{Cr}(\text{OH})_3$  so readily, and it is apt to oxidize some of the manganese to  $\text{NaMnO}_4$  (especially if there is not a sufficient excess of  $\text{NaOH}$  present).

## ANALYSIS OF THE ALUMINUM-GROUP.

TABLE VI.—ANALYSIS OF THE ALUMINUM-GROUP.

FILTRATE FROM THE SODIUM HYDROXIDE AND PEROXIDE TREATMENT:

 $\text{Na}_2\text{ZnO}_2$ ,  $\text{NaAlO}_2$ ,  $\text{Na}_2\text{CrO}_4$ . Acidify with  $\text{HNO}_3$ , add  $\text{NH}_4\text{OH}$  (P. 53).

Precipitate: $\text{Al}(\text{OH})_3$ . Dissolve in $\text{HCl}$ , add ether, pass in $\text{HCl}$ gas (P. 54).  White precipitate: $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ .	Filtrate. Add $\text{HAc}$ and $\text{BaCl}_2$ (P. 55).	
	Precipitate: $\text{BaCrO}_4$ . Dissolve in dilute $\text{HNO}_3$ , add ether and $\text{H}_2\text{O}_2$ (P. 56).	Filtrate: Zinc salt. Pass in $\text{H}_2\text{S}$ (P. 57).
	Blue coloration of ether layer: $\text{H}_3\text{CrO}_7$ .	White precipitate: $\text{ZnS}$ . Dissolve in $\text{HNO}_3$ , add $\text{Co}(\text{NO}_3)_2$ and $\text{Na}_2\text{CO}_3$ , ignite (P. 57).  Green residue: $\text{ZnO} \cdot x\text{CoO}$ .

**Procedure 53.**—*Separation of Aluminum from Chromium and Zinc.*—Acidify the alkaline solution (P. 52) with  $\text{HNO}_3$  (s.g., 1.42), avoiding a large excess; add  $\text{NH}_4\text{OH}$  until the mixture after shaking smells of it, and then add 2–3 cc. more. Heat almost to boiling in order to coagulate the precipitate, filter, and wash thoroly with hot water. (White flocculent precipitate, presence of ALUMINUM; color, less solution, absence of CHROMIUM.) (Precipitate, P. 54; filtrate—P. 55.)

*Notes.*—1. The alkaline solution is acidified with  $\text{HNO}_3$ , instead of with  $\text{HCl}$ , because the latter acid might reduce chromic acid, especially if a large quantity were added, or if the acid solution were heated. A moderate excess of  $\text{NH}_4\text{OH}$  must be added in order to keep the zinc in solution, which it does because of the production of the complex cation  $\text{Zn}(\text{NH}_3)_4^{++}$ ; but a large excess is to be avoided, since it dissolves  $\text{Al}(\text{OH})_3$ , owing to formation of  $\text{NH}_4^+\text{AlO}_2^-$ . The zinc is dissolved even when carbonate or phosphate is present.

2. Since aluminum and silica are very likely to be present in the  $\text{NaOH}$  and  $\text{Na}_2\text{O}_2$  used as reagents, and since they may be taken up from the dishes, a blank test for these impurities should be made whenever new reagents are employed for the first time, by following P. 52 and P. 53 and comparing the  $\text{NH}_4\text{OH}$  precipitate with that obtained in the actual analysis. It is also well at the same time to test for zinc by acidifying the  $\text{NH}_4\text{OH}$  solution with acetic acid and following P. 57.

3. Even when less than 1 mg. Cr is present as chromate, it imparts a distinct yellow color to the alkaline solution, so that when a colorless solution results it proves the absence of this element.

**Procedure 54.—Confirmatory Test for Aluminum.**—Dissolve the precipitate (P. 53) by pouring a hot 5–10 cc. portion of HCl repeatedly through the filter, using another portion of acid if necessary. Place the solution in a small flask. Add to it a volume of ether equal to one and one-half times that of the solution; and pass into it HCl gas until a single layer results and until fumes of HCl are copiously evolved, keeping the flask cool during the process. Cover the flask, and let the mixture stand 15 minutes. (White crystalline precipitate, presence of ALUMINUM.)

*Notes.*—1. A confirmatory test for aluminum should always be tried when the  $\text{NH}_4\text{OH}$  precipitate is small; for the precipitation by  $\text{NH}_4\text{OH}$  of an element whose hydroxide is soluble in NaOH is not very characteristic (lead, antimony, tin, and silicon showing a similar behavior). It is especially necessary to guard against mistaking  $\text{SiO}_2 \cdot \text{H}_2\text{O}$  for  $\text{Al}(\text{OH})_3$ ; for the former substance, if not entirely removed by proper dehydration in the process of preparing the solution, may appear at this point.

2. Aluminum chloride,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , is only slightly soluble in concentrated HCl solutions, and the precipitation is complete when ether is added and the mixture saturated with HCl. 0.5 mg. of aluminum can be easily detected in 30 cc. The test is therefore a delicate one. It is also characteristic; for neither silicon nor zinc nor any of the rarer elements soluble in excess of NaOH give a precipitate under the same conditions. Chromium gives a violet precipitate, but only when more than 10–20 mg. of it are present.

3. The HCl gas may be readily prepared by dropping  $\text{H}_2\text{SO}_4$  (s.g., 1.84) from a separating funnel into a bottle containing commercial HCl (s.g., 1.20).

**Procedure 55.—Detection of Chromium.**—Acidify the  $\text{NH}_4\text{OH}$  solution (P. 53) with HAc, avoiding an excess of more than 2 cc.

If the solution is colorless, treat it by P. 57.

If it is at all yellow, add about 10 cc.  $\text{BaCl}_2$  solution, allow the mixture to stand for at least 5 minutes, and filter. (Yellow precipitate, presence of CHROMIUM.) (Precipitate, P. 56; filtrate, P. 57.)

*Notes.*—1. The presence of less than 0.5 mg. chromium as chromate in a volume of 50 cc. makes the solution distinctly yellow; and the addition of  $\text{BaCl}_2$  is therefore unnecessary when the solution is perfectly colorless. It is to be avoided, since  $\text{BaSO}_4$  may be precipitated and has then to be removed by filtration. In doubtful cases the color of the solution should be compared with that of water. The color-test is, of course, not delicate by artificial light.

2. Since some sulfate may be present, the formation of a white precipitate with  $\text{BaCl}_2$  does not prove the presence of chromium. Whether the precipitate is pure white or yellow should therefore be carefully noted. The yellow color of a small  $\text{BaCrO}_4$  precipitate is most apparent when the precipitate has settled or when it has been collected on the filter. If there be sufficient sulfate present to obscure the yellow color of a little  $\text{BaCrO}_4$ , the confirmatory test described in the next procedure will enable the chromium to be detected.



**Procedure 56.**—*Confirmatory Test for Chromium.*—Pour repeatedly through the filter (P. 55) a hot 5–10 cc. portion of a mixture of 1 volume of HCl with 3 volumes of saturated  $\text{SO}_2$  solution. Evaporate the filtrate in a casserole almost to dryness. (Green coloration of the solution, presence of CHROMIUM.)

*Note.*—The green color of  $\text{CrCl}_3$  is intense enough to enable less than 0.5 mg. of chromium in 1 cc. of solution to be detected.

**Procedure 57.**—*Detection of Zinc.*—Warm the HAc solution (P. 55) to  $50^\circ$  or  $60^\circ$ , saturate it in a small flask with  $\text{H}_2\text{S}$ , cork the flask, and allow it to stand for 5 or 10 minutes if no precipitate separates at once. (White flocculent precipitate, presence of ZINC.)

To confirm the presence of zinc, filter through a double filter (made by folding two filter-papers together), wash with a little water, and pour a 5–10 cc. portion of  $\text{HNO}_3$  two or three times through the filter. To the solution add enough dilute  $\text{Co}(\text{NO}_3)_2$  solution to yield an amount of cobalt equal to about one-fourth of the amount of zinc estimated to be present, using, however, not less than 0.2 mg. cobalt. Evaporate in a casserole almost to dryness to expel the acid, neutralize with  $\text{Na}_2\text{CO}_3$  solution, and add about 0.5–1 cc. in excess. Evaporate to dryness, ignite gently until the purple color due to the cobalt disappears, and allow the casserole to cool. (Green color, presence of ZINC.)

*Notes.*—1.  $\text{ZnS}$  precipitates more rapidly, and in a somewhat more flocculent form, from a warm solution. Very small quantities of zinc (less than 1 mg.) may be missed unless a short time be allowed for the precipitate to coagulate; but since sulfur may then separate, the appearance of a white turbidity is not sufficient proof of the presence of zinc. The precipitate may be allowed to settle in order that the amount of zinc present may be better estimated. double filter is used, since the  $\text{ZnS}$  is apt to pass through the filter.

2. The immediate formation of a white flocculent precipitate with  $\text{H}_2\text{S}$  in an acetic acid solution is so characteristic as to be a sufficient test for zinc. Manganese is the only other element of this group that forms a light-colored sulfide, and this, owing to its greater solubility in water, does not precipitate from an acetic acid solution. The confirmatory test described in the last paragraph of the procedure is, however, useful when only a small noncoagulating precipitate which may be sulfur results, or when, owing to the presence of a small quantity of other elements, the precipitate is dark-colored.

3. The green compound obtained in the confirmatory test is doubtless a compound of cobalt and zinc oxides, perhaps cobalt zincate,  $\text{CoZnO}_2$ . This compound is formed at comparatively low temperatures in the presence of an

alkaline flux. Excess of cobalt must, of course, be avoided; for the black cobalt oxide completely obscures the green color. A somewhat larger proportion of cobalt than is recommended in the procedure may, however, be added without danger, and a much smaller proportion gives satisfactory results.

## ANALYSIS OF THE IRON-GROUP.

TABLE VII.—ANALYSIS OF THE IRON-GROUP.

## PRECIPITATE PRODUCED BY SODIUM HYDROXIDE AND PEROXIDE:

A. Phosphate absent:  $\text{MnO}(\text{OH})_2$ ,  $\text{Fe}(\text{OH})_3$ ,  $\text{Co}(\text{OH})_3$ ,  $\text{Ni}(\text{OH})_2$ ,  $\text{Ni}(\text{OH})_3$ ,  $[\text{ZnO}_2\text{H}_2]$ .B. Phosphate present: Also  $\text{BaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{FePO}_4$ ,  $\text{Ca}_3(\text{PO}_4)_2$ , etc.*Dissolve in  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$ , evaporate, heat with  $\text{HNO}_3$  and  $\text{KClO}_3$  (P. 61).*

Precipitate: $\text{MnO}_2$ . Add $\text{HNO}_3$ and sodium bismuthate (P. 62).  Violet color: $\text{HMnO}_4$ .	Solution: <i>Test a portion for phosphate with <math>(\text{NH}_4)_2\text{MoO}_4</math> (P. 63).</i> A. Phosphate absent; add $\text{NH}_4\text{OH}$ (P. 64). B. Phosphate present: add $\text{NH}_4\text{Ac}$ and $\text{FeCl}_3$ , dilute, boil (P. 65).		
	Precipitate: A. $\text{Fe}(\text{OH})_3$ . B. Basic ferric acetate and $\text{FePO}_4$ .	Filtrate: add $\text{NH}_4\text{OH}$ , pass in $\text{H}_2\text{S}$ (P. 66).	
		Precipitate: $\text{ZnS}$ , $\text{CoS}$ , $\text{NiS}$ . <i>Treat with cold dilute <math>\text{HCl}</math> (P. 67).</i>	Filtrate: $\text{Ba}$ , $\text{Ca}$ , $\text{Sr}$ , $\text{Mg}$ . <i>Treat by P. 81.</i>
		Solution: $\text{ZnCl}_2$ , $[\text{CoCl}_2]$ , $[\text{NiCl}_2]$ . Add $\text{NaOH}$ and $\text{Na}_2\text{O}_2$ (P. 67).	Residue: $\text{CoS}$ , $\text{NiS}$ .
		Solution: $\text{Na}_2\text{ZnO}_2$ . Add $\text{HAc}$ and $\text{H}_2\text{S}$ (P. 57).	Precipitate: $\text{Co}(\text{OH})_3$ , $\text{Ni}(\text{OH})_2$ -3.
		Dissolve in acid, evaporate, add $\text{NaOH}$ (P. 68).	
		White precipitate: $\text{ZnS}$ .	To one half add $\text{KNO}_2$ and $\text{HAc}$ (P. 69). Yellow precipitate: $\text{K}_3\text{Co}(\text{NO}_2)_6$ .
			To other half add $\text{KCN}$ , digest, add $\text{NaBrO}$ (P. 70). Black precipitate: $\text{Ni}(\text{OH})_3$ .

**Procedure 61.—Precipitation of Manganese.**—Transfer the  $\text{Na}_2\text{O}_2$  precipitate (P. 52) to a casserole, together with the filter if necessary, and add 5–10 cc.  $\text{HNO}_3$ . If there is still a residue, add gradually with stirring 3%  $\text{H}_2\text{O}_2$  solution, till the residue is dissolved. Filter to remove the paper, and evaporate the filtrate to 1 or 2 cc. Add 5–20 cc.  $\text{HNO}_3$  (s.g., 1.42), heat to boiling, add about 0.5 g. of powdered  $\text{KClO}_3$  and boil gently, adding more  $\text{KClO}_3$  in small portions if a large precipitate forms. (Dark brown or black precipitate, pres-

ence of MANGANESE.) Boil gently for a minute or two, and filter through an asbestos filter, made by pouring a suspension of washed asbestos over a compact wad of glass-wool in a glass funnel. Heat the filtrate to boiling, add more  $\text{KClO}_3$ , boil, and filter through the same filter if more of the precipitate separates. Wash two or three times with  $\text{HNO}_3$  (s.g., 1.42) which has previously been freed from the oxides of nitrogen by warming with a little  $\text{KClO}_3$ . Evaporate the filtrate to about 5 cc., but not further, and dilute it to 20 or 30 cc. (Precipitate, P. 62; filtrate, P. 63 and P. 64 or P. 65.)

*Notes.*—1. Pure concentrated  $\text{HNO}_3$  does not dissolve hydrated  $\text{MnO}_2$ ; but it may do so in the presence of filter-paper, whereby the  $\text{HNO}_3$  is reduced to lower oxides. The action is rapid in the presence of  $\text{H}_2\text{O}_2$ ; for the  $\text{MnO}_2$  is thereby quickly reduced to  $\text{Mn}(\text{NO}_3)_2$  with evolution of  $\text{O}_2$ .

2. By  $\text{HClO}_3$  in  $\text{HNO}_3$  solution (but not by  $\text{HNO}_3$  alone) manganous salts are rapidly oxidized to hydrated  $\text{MnO}_2$  with formation of chlorin dioxide ( $\text{ClO}_2$ ), which escapes as a yellow gas.

3. The separation of manganese in this way from the other metals of this group is entirely satisfactory with the exception that a small quantity of iron (up to 1 mg.) may be completely carried down with a large quantity (500 mg.) of manganese.

4. In filtering the  $\text{MnO}_2$  a cylindrical glass funnel with a small delivery tube is usually employed in quantitative analysis. An ordinary conical funnel is, however, satisfactory, provided the wad of glass-wool is made compact and enough asbestos is used. Filtration will, to be sure, be slow if the glass-wool is packed very tightly or if the asbestos mat is very thick, but in that case suction may be applied.

**Procedure 62.—Confirmatory Test for Manganese.**—To the whole of the  $\text{HClO}_3$  precipitate (P. 61) if it contains less than 10 mg. Mn, or to 5–10 mg. of it if it is larger, add about 5 cc.  $\text{HNO}_3$  and 50–100 mg. solid sodium bismuthate; pour the mixture into a test-tube, and allow the solid to settle. (Purple solution, presence of MANGANESE.)

*Note.*—This confirmatory test for manganese is usually superfluous, since the precipitation of  $\text{MnO}_2$  by  $\text{HClO}_3$  is highly characteristic. Sodium bismuthate is a trade name for an impure substance which consists largely of a peroxide of bismuth of unknown composition. If it is not available,  $\text{PbO}_2$  may be substituted for it; but in that case the mixture must be boiled for 2 or 3 minutes.

**Procedure 63.—Test for Phosphate.**—Add about one-tenth of the  $\text{HNO}_3$  solution (P. 61) to three or four times its volume of ammonium molybdate reagent, and heat to 60–70°. (Yellow, finely crystalline precipitate, presence of PHOSPHATE.) If there is no precipitate, or only a very small one, treat the remainder of the  $\text{HNO}_3$  solution by P. 64; otherwise by P. 65.

*Notes.*—1. Phosphate is tested for at this point because a different treatment is necessary when it is present in significant amount, in order to separate from

it alkaline-earth elements and to provide for their detection. When phosphate is not present, iron can be separated from nickel and cobalt by  $\text{NH}_4\text{OH}$  (as in P. 64); but when considerable phosphate is present, alkaline-earth elements may also be present and these would be partly or wholly precipitated by  $\text{NH}_4\text{OH}$  as phosphates. (See P. 51, Note 6.)

2. In order that the phosphate test may be delicate and may appear immediately, a large proportion of the molybdate reagent must be used and the solution must be warmed. The precipitate produced by ammonium molybdate,  $(\text{NH}_4)_2\text{MoO}_4$ , is ammonium phospho-molybdate, a complex salt of somewhat variable composition; it contains ammonium phosphate and molybdic acid, approximately in the proportion expressed by the formula  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ .

✓\* **Procedure 64.**—*Precipitation of Iron in Absence of Phosphate.*—

If phosphate is absent, make the  $\text{HNO}_3$  solution (P. 61) strongly alkaline with  $\text{NH}_4\text{OH}$ , using an excess of 3–5 cc. (Dark red precipitate, presence of IRON.) Filter, and wash the precipitate. Treat the filtrate by P. 66. Dissolve the precipitate in  $\text{HCl}$ , warming if necessary; and to the solution add 3–5 cc.  $\text{KCNS}$  solution. (Dark red color, presence of IRON.)

*Note.*—The red color obtained on adding  $\text{KCNS}$  is due to the formation of unionized ferric thiocyanate,  $\text{Fe}(\text{CNS})_3$ . This test may be made in the presence of much  $\text{HCl}$ ; for the acid  $\text{HCNS}$  is also a highly dissociated acid, which is therefore not displaced from its salt. Much  $\text{HNO}_3$  must not, however, be present; for it acts on  $\text{KCNS}$  forming  $\text{NO}_2$ , and this also gives a deep red color with  $\text{KCNS}$ . This test for iron is an extremely delicate one; and if only a faint color is obtained, the acids used in the process must be tested for iron.

**Procedure 65.**—*Detection of Iron and Removal of Phosphate when Present.*—If phosphate is present, test one-tenth of the  $\text{HNO}_3$  solution (P. 61) for iron, by evaporating it just to dryness, adding 1–2 cc.  $\text{HCl}$  (s.g., 1.20), evaporating again to decompose the  $\text{HNO}_3$ , diluting to 5 or 10 cc., and adding 5 cc.  $\text{KCNS}$  solution. (Permanent red color, presence of IRON.) To the remainder of the solution add  $\text{NH}_4\text{OH}$  until the precipitate formed by the last drop does not redissolve on shaking. If, owing to the addition of too much  $\text{NH}_4\text{OH}$ , the solution becomes alkaline or a large precipitate separates, make it distinctly acid with acetic acid. Add 5 cc. of a 50% solution of  $\text{NH}_4\text{Ac}$ , and, unless the mixture is already of a brownish-red color, add 10%  $\text{FeCl}_3$  solution, drop by drop, until such a color is produced. Add enough water to make the volume about 100 cc., boil in a 250 cc. flask for 5 minutes, adding more water if a very large precipitate separates, and let the mixture stand for a minute or two. Filter while still hot, and wash with hot water. Add 3–5 cc. more  $\text{NH}_4\text{Ac}$  solution to the filtrate, boil it again, and collect on a separate

filter any further precipitate. Reject the precipitate. Make the filtrate alkaline with  $\text{NH}_4\text{OH}$ , and treat it by P. 66.

*Notes.*—1. With regard to the test for iron with KCNS and the necessity of removing the  $\text{HNO}_3$ , see P. 64, Note.

2. This method of separation depends on the facts that, upon boiling an acetic acid solution containing much acetate, ferric iron is completely precipitated in the form of a basic acetate; and that all the phosphate present combines with the iron when it is present in excess, and therefore then passes completely into the precipitate, leaving the bivalent elements in solution. This behavior of the phosphate is due to the fact that the solubility in acids of the phosphates of the trivalent elements is much smaller than that of the phosphates of the bivalent elements.

3. If upon adding the ammonium acetate the solution becomes of a reddish color, it shows that iron is present in quantity more than sufficient to combine with the phosphate; for a cold solution containing ferric acetate is of a deep red color. If, on the other hand, a colorless solution results (either with or without a precipitate), it shows that there is no excess of iron, and  $\text{FeCl}_3$  is therefore added. This causes the precipitation of  $\text{FePO}_4$  as a yellowish white precipitate. Upon boiling, the excess of iron separates completely as a dark red gelatinous precipitate of basic ferric acetate, leaving the supernatant liquid colorless, except when nickel or cobalt is present.

4. The solution is diluted to at least 100 cc., owing to the large volume of the precipitate; and it is heated in a capacious flask, owing to its tendency to boil over.

**Procedure 66.**—*Precipitation of Nickel and Cobalt.*—Into the ammoniacal solution (P. 64 or P. 65) pass  $\text{H}_2\text{S}$  gas until the mixture after shaking blackens  $\text{PbAc}_2$  paper held above it. (Black precipitate, presence of NICKEL or COBALT.) Filter, and wash the precipitate with water containing a very little  $(\text{NH}_4)_2\text{S}$ . (Precipitate, P. 67; filtrate, to detect alkaline-earth elements, P. 81.)

*Note.*—In precipitating  $\text{NiS}$ , the use of  $\text{H}_2\text{S}$  has the advantage that the nickel is all thrown down at once, while with  $(\text{NH}_4)_2\text{S}$  some of it usually remains in the solution, giving it a dark brown color. If  $(\text{NH}_4)_2\text{S}$  be used, the filtrate must be boiled to throw down the unprecipitated nickel, as described in P. 51.

**Procedure 67.**—*Separation of Zinc from the Nickel and Cobalt.*—Transfer the  $\text{H}_2\text{S}$  precipitate (P. 66) with the filter to a casserole, and add 10–30 cc. of a cold mixture of 1 volume  $\text{HCl}$  and 5 volumes of water. Digest in the cold for 5 minutes, stirring the mixture frequently, and filter. Treat the residue by P. 68.

Boil the  $\text{HCl}$  solution until the  $\text{H}_2\text{S}$  is completely expelled, add  $\text{NaOH}$  solution until the mixture is slightly alkaline, transfer to a casserole, cool, and add 0.5–1 g.  $\text{Na}_2\text{O}_2$ , a small portion at a time. Boil for several minutes to decompose the excess of  $\text{Na}_2\text{O}_2$ , cool the

mixture, and filter. Wash the precipitate and treat it by P. 68, uniting it with the sulfide residue undissolved by the dilute HCl. Acidify the filtrate with HAc, and test it for ZINC by P. 57.

*Notes.*—1. This treatment with dilute HCl serves to extract almost completely the zinc which may be present in this precipitate, owing to its having been carried down in the  $\text{Na}_2\text{O}_2$  precipitate as described in P. 52, Note 10. A small proportion of the nickel and cobalt present (5–20%) always dissolves in the dilute HCl, and the subsequent treatment with  $\text{Na}_2\text{O}_2$  serves to separate these elements from the zinc. This separation is satisfactory when, as in this case, the nickel and cobalt are present in small quantity; for then only an insignificant amount of zinc is carried down with them. When, therefore, the  $\text{H}_2\text{S}$  precipitate is small, it may, instead of being treated with dilute HCl, be dissolved at once in *aqua regia* and the solution treated directly as described in the last paragraph of the procedure.

2. This procedure must always be followed in order to determine whether or not zinc is present in the substance, unless a satisfactory test for it has already been obtained in P. 57, or unless the original  $\text{Na}_2\text{O}_2$  precipitate (P. 52) was small.

**Procedure 68.**—*Solution of the Nickel and Cobalt Precipitates.*—Transfer the sulfide residue undissolved by dilute HCl and the  $\text{Na}_2\text{O}_2$  precipitate (P. 67), with the filters to a casserole, add 5–15 cc. HCl and a few drops  $\text{HNO}_3$ , warm until the black precipitate is dissolved, and filter off the paper. Evaporate the solution nearly to dryness to expel most of the acid, add about 5 cc. water, and then NaOH solution, drop by drop, until the mixture is neutral, or until a permanent precipitate just forms. Test one-half of this mixture for COBALT by P. 69, and the remainder for NICKEL by P. 70.

**Procedure 69.**—*Detection of Cobalt.*—To one-half of the neutral solution (P. 68) add 15 cc. HAc and then 50 cc. 30%  $\text{KNO}_2$  solution; dilute to 100 cc., and allow the mixture to stand at least half an hour if no precipitate forms sooner. (Yellow, finely divided precipitate, presence of COBALT.) Filter, and wash with  $\text{KNO}_2$  solution. If the precipitate is very small, incinerate the filter. Introduce a portion of the precipitate, or of the ash, into a borax bead made in the loop of a platinum wire, and heat strongly, adding more of the precipitate or ash if no color is obtained. (Deep blue color, presence of COBALT.)

*Notes.*—1. The precipitate is potassium cobaltic nitrite,  $3\text{KNO}_2 \cdot \text{Co}(\text{NO}_2)_3$ , or more properly, potassium cobaltinitrite,  $\text{K}_3\text{Co}(\text{NO}_2)_6$ , since in solution it dissociates into  $\text{K}^+$  and the complex anion  $\text{Co}(\text{NO}_2)_6^{3-}$ . In the formation of this substance the cobaltous salt is oxidized to the cobaltic state by the nitrous acid displaced from its salt by the acetic acid, the cobaltic salt combining as fast as formed with the potassium nitrite.

2. The precipitate is somewhat soluble in water, but very difficultly soluble in a concentrated  $\text{KNO}_2$  solution, owing to the common-ion effect of the potas-

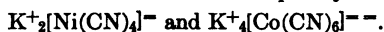
sium-ion. The formation of the  $K_3Co(NO_2)_6$  precipitate takes place slowly; but, even when only 0.1–0.2 mg. Co is present, a distinct precipitate is obtained within 10 minutes. The complete precipitation of a large amount of cobalt, however, requires several hours, so that the method is ill adapted for the removal of cobalt before testing for nickel. Moreover, when nickel is present, some of it is carried down with the cobalt; and this is true even when the total amount of nickel is small. For these reasons the test for nickel is made in a separate portion.

3. Nickelous salts are not oxidized by nitrous acid, and are not precipitated by  $\text{KNO}_3$  except in a very concentrated solution, when a dark-yellow or dark-red precipitate of potassium nickelous nitrite,  $\text{K}_4\text{Ni}(\text{NO}_2)_6$ , may separate. By making the volume large, as directed in the procedure, there is no danger of the precipitation of nickel.

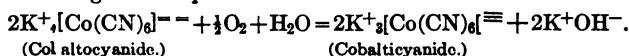
**Procedure 70.**—*Detection of Nickel.*—To the remainder of the neutralized solution (P. 68) add KCN solution, a few drops at a time, until all or nearly all of any precipitate that may form at first redissolves; then add 0.5–3 cc. more (according to the amount of the KCN precipitate). Heat to 50 or 60° in an open casserole, with frequent stirring, for 5 minutes, or longer if the solution has not become light-colored. Filter off and reject any small precipitate that may remain. To the filtrate, preferably in a test-tube, add freshly prepared, concentrated NaBrO solution (see Note 3) until a piece of filter-paper moistened with KI and starch solutions, when dipped into the solution, is colored blue or brown. Allow the mixture to stand 5–10 minutes and filter. (Brown to black precipitate, presence of NICKEL.)

Wash the precipitate; dissolve it, or a small portion of it if it is large, in 2-3 cc.  $\text{HNO}_3$ ; add 3-5 cc. 10% tartaric acid solution, neutralize with  $\text{NaOH}$  solution, and add 3 or 4 cc. in excess. Pass in  $\text{H}_2\text{S}$  gas for about 1 minute, filter out any precipitate that may form, and saturate the filtrate with  $\text{H}_2\text{S}$ . Filter again if there is a precipitate. (Brown coloration, presence of NICKEL.)

*Notes.*—1. The reactions involved in the first test for nickel are as follows: When a little KCN is added to the neutral solution, precipitates of (green)  $\text{Ni}(\text{CN})_2$  and (dark brown)  $\text{Co}(\text{CN})_2$  result, unless only small amounts of these elements are present. The addition of more KCN causes the precipitate to dissolve, owing to the formation of soluble complex cyanides, such as



The complex nickel salt is stable in the air, but the cobalt salt oxidizes very readily according to the equation:



The first action of the NaBrO is to decompose the excess of KCN, chiefly with formation of KCNO. It then oxidizes the nickel to the nickelic state, which



is then immediately precipitated as brownish-black  $\text{Ni(OH)}_3$  by the  $\text{NaOH}$  present. The cobalt, tho already in the cobaltic state, is not precipitated as  $\text{Co(OH)}_3$ , because the complex ion  $[\text{Co(CN)}_6]$  is so slightly ionized into its constituent-ions ( $\text{Co}^{+++}$  and  $\text{CN}^-$ ) that the concentration of the  $\text{Co}^{+++}$  does not suffice, with the  $\text{OH}^-$  present, to supersaturate the solution with  $\text{Co(OH)}_3$ .

2. In executi~~ng~~g this procedure the following precautions should be observed: A very large excess of the strong  $\text{KCN}$  solution over that required to redissolve the precipitate should not be added; for the excess must be destroyed by the  $\text{NaBrO}$  before the nickel can be oxidized and precipitated by it. Yet there must be sufficient  $\text{KCN}$  added, not only to combine with all the cobalt, but to furnish a moderate excess in order that the oxidati~~on~~ to the cobalticyanide may take place rapidly. Care must also be taken to heat the solution long enough in the air to complete this oxidation before the  $\text{NaBrO}$  is added; for otherwise the latter reagent after destroying the free  $\text{KCN}$  will oxidize the decomposable cobaltocyanide with precipitation of  $\text{Co(OH)}_3$ , just as it does the nickelocyanide. The completion of the oxidation by the air is indicated by the disappearance of the dark color in the solution. Finally, one must make sure (by applying the iodide-starch test) that an excess of  $\text{NaBrO}$  over that required to oxidize both the cyanide and the nickel has been added. If these precautions are observed, there is no difficulty in securing a precipitate with 0.2 mg. of nickel nor in causing 300 mg. of cobalt to remain entirely in solution.

3. The hypobromite reagent is prepared by adding liquid bromin to a known volume of  $\text{NaOH}$  solution until the solution becomes distinctly red, owing to the presence of excess of bromin; and then adding half as much more  $\text{NaOH}$  solution. This solution may be filtered through a hardened filter. It decomposes fairly rapidly, with formation of bromate and bromide, and also with evolution of oxygen, and should therefore not be used when more than a few days old.

4. When an alkaline tartrate solution containing a small amount of nickel (even 0.1-0.2 mg. in 20 cc.) is saturated with  $\text{H}_2\text{S}$ , a clear brown solution is obtained. With somewhat larger amounts of nickel (10-20 mg.) the liquid is opaque, but runs through a filter very readily. The condition of the nickel in this solution is not known. The presence of the tartrate serves merely to prevent the precipitation of  $\text{Ni(OH)}_2$  by the  $\text{NaOH}$  solution, owing to the formation of a complex salt containing the nickel in the anion. The brown color does not appear until the alkaline solution is nearly saturated with  $\text{H}_2\text{S}$ , so that care must be taken to use an excess of  $\text{H}_2\text{S}$ .

5. This confirmatory test for nickel is not interfered with by moderate amounts of other elements of this group, such as cobalt and iron; for on leading  $\text{H}_2\text{S}$  into an alkaline tartrate solution containing these elements, they are completely precipitated as sulfides and may be filtered off, yielding a filtrate which in the absence of nickel remains clear when saturated with  $\text{H}_2\text{S}$ , or becomes dark brown when it is present in even small amount.

## PRECIPITATION AND ANALYSIS OF THE ALKALINE-EARTH GROUP.

TABLE VIII.—ANALYSIS OF THE ALKALINE-EARTH GROUP.

AMMONIUM CARBONATE PRECIPITATE: $\text{BaCO}_3$ , $\text{SrCO}_3$ , $\text{CaCO}_3$ , $\text{MgCO}_3$ , $(\text{NH}_4)_2\text{CO}_3$ . <i>Dissolve in HAc, add <math>\text{K}_2\text{CrO}_4</math> (P. 82).</i>			
Precipitate: $\text{BaCrO}_4$ . <i>Dissolve in HCl,            test in flame            (P. 83).</i> <hr/> Green color: Ba.	Filtrate. <i>Add <math>\text{NH}_4\text{OH}</math> and alcohol (P. 84).</i>		
	Precipitate: $\text{SrCrO}_4$ . <i>Confirm by            P. 85.</i>	Filtrate: Ca and Mg salts. <i>Dilute, add <math>(\text{NH}_4)_2\text{C}_2\text{O}_4</math> (P. 86).</i>	
		Precipitate: $\text{CaC}_2\text{O}_4$ . <i>Dissolve in dilute  <math>\text{H}_2\text{SO}_4</math>, add alcohol            (P. 87).</i>	Filtrate. <i>Add <math>\text{NH}_4\text{OH}</math>            and <math>\text{Na}_2\text{HPO}_4</math>            (P. 88).</i>
			Precipitate: $\text{MgNH}_4\text{PO}_4$ .

**Procedure 81.**—*Precipitation of the Alkaline-Earth Group.*—Evaporate the filtrate from the  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{S}$  precipitate (P. 51) to a volume of about 10 cc., and filter off the sulfur

To the cold solution add 30 cc.  $(\text{NH}_4)_2\text{CO}_3$  reagent and 30 cc. 95% alcohol; let the mixture stand for at least half an hour, shaking frequently. (Precipitate, presence of ALKALINE-EARTH ELEMENTS.) Filter and wash the precipitate with a little  $(\text{NH}_4)_2\text{CO}_3$  reagent; if the precipitate is large, dry it by suction. (Precipitate, P. 82; filtrate, P. 91.)

*Notes.*—1. The filtrate from the  $(\text{NH}_4)_2\text{S}$  precipitate is evaporated in order that the elements of the alkaline-earth group may be precipitated more quickly and more completely. The volume to which the  $(\text{NH}_4)_2\text{CO}_3$  reagent is added should not exceed 20 cc. The evaporation also serves to destroy  $(\text{NH}_4)_2\text{S}$  and to coagulate any sulfur that may separate.

2. The reagent used in precipitating the elements of this group is conveniently prepared by dissolving 100 g. freshly powdered ammonium carbonate in 300 cc. 6-normal  $\text{NH}_4\text{OH}$ , filtering if there is any precipitate, and adding 100 cc. concentrated  $\text{NH}_4\text{OH}$  (s.g., 0.90).

3. If the ammonium carbonate and hydroxide were added in only small excess, the precipitation of  $\text{CaCO}_3$ ,  $\text{SrCO}_3$ , and  $\text{BaCO}_3$  would not be complete, and additional tests for small quantities of these elements would have to be made in the filtrate. But, by the use of a concentrated solution of  $(\text{NH}_4)_2\text{CO}_3$  containing a large excess of  $\text{NH}_4\text{OH}$  (so as to diminish the hydrolysis of the carbonate into  $(\text{NH}_4)^+\text{HCO}_3^-$  and  $\text{NH}_4\text{OH}$ ), the pre-

cipitation may be made practically complete, owing to the greatly increased concentration of carbonate-ion ( $\text{CO}_3^{2-}$ ).

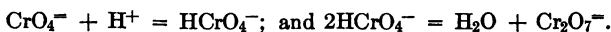
4. When the concentrations of  $(\text{NH}_4)_2\text{CO}_3$  and  $\text{NH}_4\text{OH}$  are sufficiently great, magnesium is in the cold also completely precipitated. The precipitate, which is in this case a double carbonate,  $\text{MgCO}_3 \cdot (\text{NH}_4)_2\text{CO}_3 \cdot 4\text{H}_2\text{O}$ , is, however, fairly soluble in cold water and readily soluble in hot water.

5. From a cold aqueous solution the precipitation of these elements takes place slowly, especially in the case of magnesium and calcium; but it is greatly accelerated by the addition of alcohol and by shaking. Under the conditions recommended in the procedure 0.5 mg. of any of the four elements is easily detected within half an hour.

**Procedure 82.—Precipitation of Barium.**—Dissolve the  $(\text{NH}_4)_2\text{CO}_3$  precipitate (P. 81) by pouring repeatedly through the filter a 10–25 cc. portion of hot HAc. Make the solution slightly alkaline with  $\text{NH}_4\text{OH}$ ; add HAc, drop by drop, until the solution becomes barely acid to litmus, and then add 3 cc. more. Dilute the solution to 40 cc., and heat it to boiling in a flask. Measure out 10 cc. 20%  $\text{K}_2\text{CrO}_4$  solution, and add it a few drops at a time, heating and shaking after each addition. Finally, heat the mixture at 90–100° for 1 or 2 minutes, shaking at the same time. Filter, even tho the solution appear clear; remove the filtrate, and wash the precipitate thoroly with cold water. (Pale yellow precipitate, presence of BARIUM.) (Precipitate, P. 83; filtrate, P. 84.)

*Notes.*—1. The solubility in water of the chromates of the alkaline-earth elements increases rapidly in the order, Ba, Sr, Ca, Mg. The difference in solubility of  $\text{BaCrO}_4$  and  $\text{SrCrO}_4$  is so great that under the conditions of the procedure 0.5 mg. Ba can be detected, while even 400 mg. Sr give no precipitate. The amount of  $\text{K}_2\text{CrO}_4$  added is sufficient to precipitate completely more than 500 mg. of barium.

2. Acetic acid is added to increase the solubility of  $\text{SrCrO}_4$ . By its action the concentration of the chromate-ion is reduced, owing to its conversion partly into hydrochromate-ion and partly into bichromate-ion, according to the reactions:



It is evident that the  $\text{CrO}_4^{2-}$  concentration must decrease as the  $\text{H}^+$  concentration increases. For this reason the presence of an excess of a largely ionized acid (such as HCl or  $\text{HNO}_3$ ) would prevent the precipitation of  $\text{BaCrO}_4$ ; but since acetic acid is a slightly ionized acid, and since a large amount of acetate is present, the addition of a considerable excess of acetic acid has but little effect.

3. The  $\text{K}_2\text{CrO}_4$  is added slowly to the hot solution and the mixture is shaken and heated in the neighborhood of 100° before filtering, since otherwise the precipitate is liable to pass through the filter. By this method of precipitation almost all the barium is precipitated before an excess of  $\text{K}_2\text{CrO}_4$  is added. This is of importance since, when much barium is present, as much as 3 mg. Sr may be carried down completely if the  $\text{K}_2\text{CrO}_4$  reagent is added quickly.

If for any reason the filtrate is turbid after two or three filtrations, the precipitate may be coagulated by boiling gently for 1 or 2 minutes. Vigorous or long-continued boiling is to be avoided, since, owing to loss of acetic acid,  $\text{SrCrO}_4$  may then separate if much strontium is present. When less than 1 mg. Ba is present it is very difficult to distinguish the faint turbidity in the colored solution; but the pale yellow precipitate can be seen after filtering and washing the  $\text{K}_2\text{CrO}_4$  out of the filter. The precipitate must be washed thoroly, in order to remove strontium as completely as possible, which otherwise would obscure the confirmatory test for barium.

**Procedure 83.**—*Confirmatory Test for Barium.*—Dissolve the  $\text{K}_2\text{CrO}_4$  precipitate (P. 82) in  $\text{HCl}$ , and evaporate the solution to a few drops. Dip a clean platinum wire into the solution, and introduce the wire into a colorless flame. (Green flame, presence of **BARIUM.**)

*Note.*—When the amount of barium is very small, only a momentary green color is seen as the yellow (sodium) color which first appears fades away. The only other elements that give a green color to the flame are copper and thallium. Strontium gives a crimson color.

**Procedure 84.**—*Precipitation of Strontium.*—To the filtrate (P. 82), after cooling it, add  $\text{NH}_4\text{OH}$  (s.g., 0.90) slowly until the color of the solution changes from orange to yellow, and then 3 cc. more. Dilute the solution to 60 cc., and add slowly, with constant shaking, 50 cc. 95% alcohol. (Pale yellow precipitate, presence of **STRONTIUM.**) Filter after several minutes, using suction if the filtration is slow; but do not wash the precipitate. [To ensure the complete precipitation of strontium when much strontium or barium has been found, add to the filtrate 5 cc. 20%  $\text{K}_2\text{CrO}_4$  solution and 10 cc. alcohol; filter off any precipitate that separates, and reject it if a precipitate has already been obtained in this procedure.] (Precipitate, P. 85; filtrate, P. 86.)

*Note.*—Under these conditions 0.5 mg. of strontium gives a precipitate almost at once; while even 400–500 mg. of calcium or magnesium do not do so. A moderate change in the conditions will not affect this result; but if the concentration of alcohol or  $\text{K}_2\text{CrO}_4$  is much less than is recommended, the precipitation of strontium may be incomplete; while the addition of larger amounts of alcohol and  $\text{K}_2\text{CrO}_4$  may cause the precipitation of chromate of calcium or magnesium if much of these elements is present, or of  $\text{K}_2\text{CrO}_4$  itself, since the latter is not very soluble in alcohol. The confirmatory test should therefore be tried. The precipitate is not washed, because  $\text{SrCrO}_4$  is a fairly soluble substance.

**Procedure 85.**—*Confirmatory Test for Strontium.*—Transfer the precipitate (P. 84), with the filter if necessary, to a casserole; add 30–35 cc. of the oxalate-carbonate-chromate mixture (see Note 1);

cover the casserole with a watch glass, and boil gently for 3–5 minutes. Filter, wash the precipitate thoroly with water, and pour repeatedly through the filter about 5 cc. 1-normal HAc. Make the solution alkaline with  $\text{NH}_4\text{OH}$ , add 3–5 cc. of the  $(\text{NH}_4)_2\text{CO}_3$  reagent, heat to boiling, and set aside for 5–10 minutes. (White precipitate, presence of STRONTIUM.)

*Notes.*—1. The oxalate-carbonate-chromate mixture here referred to is prepared by dissolving 30 g.  $\text{Na}_2\text{C}_2\text{O}_4$ , 6 g.  $\text{Na}_2\text{CO}_3$ , and 3 g.  $\text{K}_2\text{CrO}_4$  in 1 liter of water.

2. The proportions of oxalate, carbonate, and chromate in this mixture are so chosen that  $\text{CaCrO}_4$  (if present) is converted into  $\text{CaC}_2\text{O}_4$ , that  $\text{SrCrO}_4$  is converted into  $\text{SrCO}_3$ , and that  $\text{BaCrO}_4$  remains unchanged. Hence, when the residue is subsequently treated with dilute HAc, only the strontium salt dissolves, since  $\text{CaC}_2\text{O}_4$  and  $\text{BaCrO}_4$  are nearly insoluble in this acid.

3. The behavior of each of the three elements towards the mixture is determined by the relative solubilities of its oxalate, carbonate, and chromate in water. In the case of calcium, the chromate is readily soluble, while the carbonate and oxalate have a very slight solubility, which is not far from the same in the two cases. By making the oxalate concentration four or five times as great as the carbonate concentration in the mixture, the complete conversion of  $\text{CaCrO}_4$  or  $\text{CaCO}_3$  into  $\text{CaC}_2\text{O}_4$  is assured. In the case of strontium, the carbonate is much less soluble than the oxalate or chromate, so that even if the proportion of oxalate or chromate in the mixture were made twice as great as directed, all the strontium would still be found in the form of  $\text{SrCO}_3$ . In the case of barium, the chromate is so much less soluble than the carbonate or oxalate that even the small proportion of chromate in the mixture prevents the conversion of  $\text{BaCrO}_4$  into  $\text{BaCO}_3$  or  $\text{BaC}_2\text{O}_4$ .

4. The procedure is delicate enough to enable 0.5 mg. Sr to be detected, while even 30 mg. Ca (or Mg) give no indication of their presence. If more calcium than this were present in the  $\text{K}_2\text{CrO}_4$  precipitate, a very small precipitate of  $\text{CaCO}_3$  might result on adding  $(\text{NH}_4)_2\text{CO}_3$ .

**Procedure 86.**—*Precipitation of Calcium.*—To the filtrate (P. 84) add 200 cc. water; heat to boiling, and add slowly to the boiling solution 20–50 cc.  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution; shake, and let the mixture stand for several minutes. (White precipitate, presence of CALCIUM.) Filter, and wash the precipitate once with water. (Precipitate, P. 87; filtrate, P. 88.)

*Note.*—The solution is heated to boiling, the ammonium oxalate is added slowly, and the mixture is allowed to stand a few minutes, since otherwise the filtration is slow and  $\text{CaC}_2\text{O}_4$  may pass through the filter. Moreover, since small amounts of calcium do not precipitate rapidly in the cold, 2 or 3 mg. may escape detection if the mixture is not heated. Under the conditions of the procedure, *i. e.*, in a volume of about 300 cc., 0.5 mg. Ca gives a precipitate within 5 minutes, while 400 mg. Mg do not. If, however, the volume of the solution is much less than 300 cc. and much magnesium is present, some may precipitate, especially if the mixture be allowed to cool to room temperature.

**Procedure 87.—Confirmatory Test for Calcium.**—Treat the  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  precipitate (P. 86) with 5 cc. cold  $\text{H}_2\text{SO}_4$ ; filter if necessary; add 10–15 cc. 95% alcohol, and let the mixture stand for several minutes. (White precipitate, presence of CALCIUM.)

*Note.*—1.  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  is very difficultly soluble in water, but dissolves in dilute solutions of largely ionized acids, owing to the formation by metathesis of unionized  $\text{HC}_2\text{O}_4^-$ .  $\text{CaSO}_4$  is somewhat soluble in dilute  $\text{H}_2\text{SO}_4$ , but is completely thrown out as a flocculent precipitate by the addition of 2 or 3 volumes of alcohol. 1 mg. Ca gives a distinct turbidity at once, 0.5 mg. in 1–3 minutes, and 0.2 mg. within 10 minutes. Even a large amount of magnesium does not interfere with the test. If strontium were present, a small amount of it would dissolve in the  $\text{H}_2\text{SO}_4$ , but only enough to give a slight turbidity on the addition of alcohol, corresponding to that given by 0.2–0.3 mg. Ca. calcium after standing a few minutes. Therefore anything more than a slight turbidity is a conclusiv proof of the presence of calcium.

**Procedure 88.—Detection of Magnesium.**—To the filtrate from the  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  precipitate (P. 86) add 10 cc.  $\text{NH}_4\text{OH}$  (s.g., 0.90) and 20 cc.  $\text{Na}_2\text{HPO}_4$  solution; cool, and shake the mixture; if no precipitate forms, let the mixture stand for at least half an hour, shaking it frequently. (White precipitate, presence of MAGNESIUM.)

*Note.*—This test for magnesium depends upon the precipitation of magnesium ammonium phosphate,  $\text{Mg}(\text{NH}_4)\text{PO}_4$ . This salt is slightly soluble even in cold water, owing chiefly to hydrolysis into  $\text{Mg}(\text{OH})_2$  and  $\text{Mg}^{++}\text{HPO}_4^-$ ; and the test is therefore made in a strongly ammoniacal solution. Since the solubility increases rapidly with the temperature, the solution is cooled to the room temperature, or below. In an aqueous solution this substance shows a great tendency to form a supersaturated solution, and it is therefore usually directed to make the test in as small a volume as possible. In the presence of alcohol, however, precipitation takes place rapidly, and even 0.5 mg. Mg gives a distinct turbidity in a solution containing 250 cc. water and 50 cc. alcohol within half an hour. A small precipitate of this kind settles out on further standing and may then be detected by rotating the solution so as to cause the precipitate to collect in the center. Even so small an amount as 3 mg. Ca gives a distinct precipitate of calcium phosphate; it is therefore essential that the calcium be completely precipitated in P. 86.

## ANALYSIS OF THE ALKALI-GROUP.

TABLE IX.—ANALYSIS OF THE ALKALI-GROUP.

FILTRATE FROM AMMONIUM CARBONATE PRECIPITATE:  $\text{NH}_4$ , K, Na salts.*Add  $\text{H}_2\text{SO}_4$ , evaporate to dryness (P. 91).*

Vapor: $\text{NH}_4$ salts.	Residue: $\text{K}_2\text{SO}_4$ , $\text{Na}_2\text{SO}_4$ . Add 3 cc. water (P. 91).	
	<i>To one-third of the solution add <math>\text{Na}_3\text{Co}(\text{NO}_2)_6</math> (P. 92).</i>	<i>To the remainder add <math>\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7</math> (P. 93).</i>
	Yellow precipitate: $\text{K}_2\text{NaCo}(\text{NO}_2)_6$ . <i>Test in flame, view through blue glass.</i>	Crystalline precipitate: $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$ ; <i>Test in flame.</i>
	Violet color: K.	Yellow color: Na.

**Procedure 91.—Removal of Ammonium Salts.**—Evaporate the filtrate from the  $(\text{NH}_4)_2\text{CO}_3$  precipitate (P. 81) almost to dryness; add 3–5 cc.  $\text{H}_2\text{SO}_4$ ; evaporate to dryness in a small casserole, and ignite the residue, at first gently, then at dull redness, until no more white fumes come off, taking care to heat the sides as well as the bottom of the dish. After the dish has become cold add 3 cc. cold water, and filter through a very small filter. Test one-third of the filtrate for potassium by P. 92; test the remainder of the filtrate for sodium by P. 93.

*Notes.*—1. Great care must be taken to remove the ammonium salts completely, since even 1 mg.  $\text{NH}_4$  would give a precipitate in the subsequent test for potassium.

2. A brown or black residue of organic matter, coming from impurity in the ammonium salts added in the course of analysis and from the alcohol and filter paper, may remain upon treating the ignited residue with water. Sometimes, owing to the presence of this organic matter, the aqueous solution after ignition has a brown or yellow color. In such a case the color may be destroyed by adding 1–2 cc.  $\text{H}_2\text{SO}_4$  (s.g., 1.84) and 1 cc.  $\text{HNO}_3$  (s.g., 1.42), evaporating till white fumes of  $\text{H}_2\text{SO}_4$  begin to come off, again adding  $\text{HNO}_3$  (s.g., 1.42) and evaporating, repeating these operations till the  $\text{H}_2\text{SO}_4$  becomes light-colored, and finally igniting to expel all the  $\text{H}_2\text{SO}_4$ .

3. Only 3 cc. of cold water are added to the ignited residue, in order that the volume may be small enough to enable the subsequent test for sodium to be applied directly, and in order to leave undissolved a part of the  $\text{K}_2\text{SO}_4$  if a large quantity of potassium is present. For the sodium test is more delicate, the less the quantity of potassium salt present.

**Procedure 92.—Detection of Potassium.**—Dilute one-third of the solution (P. 91) to 3–5 cc., and add an equal volume of  $\text{Na}_3\text{Co}(\text{NO}_2)_6$  reagent. If no precipitate forms at once, let the mixture stand for at least 15 minutes. Filter, and wash the precipitate thoroly with water. (Yellow precipitate, presence of POTASSIUM.)

Dissolve the precipitate in hot dilute HCl, evaporate to a few drops, dip a clean platinum wire into the solution, and introduce it into a colorless gas flame, viewing the flame through a sufficient thickness of blue cobalt glass to cut off sodium light. (Violet flame, presence of POTASSIUM.)

*Notes.*—1. The presence of 0.3 mg. K in 5 cc. of solution may be detected within 5 or 10 minutes, and an even smaller amount on long standing. The yellow color of the precipitate is best seen on the filter after washing out the  $\text{Na}_3\text{Co}(\text{NO}_2)_6$  thoroly. In the presence of even 0.5–1.0 mg.  $\text{NH}_4$  a precipitate is obtained very similar in appearance to that obtained with potassium; but moderate amounts of the alkaline-earth elements do not interfere with the test.

2. The flame-test for sodium is so much more delicate than that for potassium that the yellow color due to a trace of sodium may completely obscure the color given by a moderate amount of potassium. A sufficient thickness of blue cobalt glass is used to absorb the yellow rays completely, and thus permit the violet rays due to potassium to be seen. Comparative experiments with known solutions ought always to be made, unless the analyst is perfectly familiar with the appearance of the flames.

**Procedure 93.—Detection of Sodium.**—To the remainder of the solution (P. 91), which should have a volume of 1–2 cc., add 1–2 cc.  $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7$  reagent; pour the mixture into a test-tube, and let it stand for at least half an hour, or better over night. (White crystalline precipitate, presence of SODIUM.)

Decant off the solution, wash the precipitate several times with water, and dissolve it in a little HCl. Evaporate the solution to a few drops, and introduce a little of it on a platinum wire into a colorless gas flame. (Brilliant yellow flame, presence of SODIUM.)

*Notes.*—1. The dipotassium dihydrogen pyroantimonate ( $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7$ ) reagent is prepared as follows: Add 2 g. of the best commercial salt to 100 cc. boiling water, boil for about 1 minute until nearly all the salt is dissolved, quickly cool the solution, add about 3 cc. 10% KOH solution, and filter. If a (flocculent) precipitate settles out on standing, decant off the clear solution. —This reagent will usually keep for several months, but it should be tested frequently with a known solution of a pure sodium salt. When a pyroantimonate solution is made slightly acid, it decomposes rapidly with precipitation of metantimonic acid. The same reaction takes place slowly in neutral solutions, owing to hydrolysis.

2. In this test, if 2 cc. of the antimonate reagent are added to 1 cc. of solution, 2 mg. Na give a distinct crystalline precipitate in less than 5 minutes,



1 mg. within 30 minutes, and a smaller amount on standing several hours. The precipitate is a heavy crystalline, granular one, and usually adheres in part to the glass, where it can best be seen by tilting the test-tube. Altho in a solution of a pure sodium salt 1 mg. Na is easily detected, yet in an actual analysis, owing to the presence of potassium salt, it is often difficult to detect less than 2-3 mg. Moreover, certain other elements, even if present in small quantity, giv precipitates; thus a distinct turbidity is produced by even 0.1-0.2 mg. Ca, Ba, or Mg, and by 1-2 mg. Al. These elements giv, however, light, flocculent precipitates which are, very different from the heavy crystalline precipitate obtained with sodium, especially if the mixture has been allowed to stand a few hours. The crystals of the sodium salt may be separated from a flocculent precipitate by shaking the mixture, waiting long enough for the heavy crystals to settle, and decanting off the suspended, flocculent precipitate.

3. In the flame-test the yellow color is to be regarded as a confirmation of the presence of an appreciable amount of sodium in the sample only when a brilliant, large, spreading flame is obtained. Owing to the delicacy of the test, there is always sufficient sodium present to giv a slight yellow color.

## DETECTION OF THE ACIDIC CONSTITUENTS.

## DISTILLATION WITH PHOSPHORIC ACID.

TABLE X.—BEHAVIOR OF THE ACIDIC CONSTITUENTS ON DISTILLATION WITH PHOSPHORIC ACID.

*Distil the substance with dilute  $H_3PO_4$  (P. 101). Collect the first half of the distillate in  $Ba(OH)_2$  solution and the second half in water. To the residue add Cu and distil again, collecting this third distillate in water.*

FIRST DISTILLATE	SECOND DISTILLATE	THIRD DIST.	NONVOLATIL RESIDUE
$CO_2$ from carbonate. $SO_2$ from sulfite or thiosulfate. $Cl_2$ from hypochlorite, chlorate, or chloride.* $Br_2$ from bromide.* $I_2$ from iodide.* $HNO_2$ from nitrite. $H_2S$ from sulfide. $HCN$ from cyanide.	$HCl$ from chloride. $HBr$ from bromide. $HI$ from iodide. $HSCN$ from thiocyanate. $HCN$ from ferrocyanide. $H_2S$ from insoluble sulfides. $HNO_3$ from nitrate. $Cl_2$ from chlorate or chloride*. $Br_2$ from bromide.* $I_2$ from iodide.	$SO_2$ from sulfate.	$HPO_3$ from phosphate. $HBO_2$ from borate. $H_2SiO_3$ (as a precipitate) from silicate.

\* When the substance contains also an oxidizing compound.

**Procedure 101.**—*Distillation with Phosphoric Acid.*—Place 2 g. of the finely powdered substance and a few glass beads in a 100 cc. round-bottom Jena-glass flask fitted with a rubber stopper, through which pass a straight tube, 20–30 cm. long, leading to the bottom of the flask and a delivery tube. Fasten the flask in an inclined position. Lead the end of the delivery tube through a two-hole stopper into 40 cc. of nearly saturated  $Ba(OH)_2$  solution contained in a 100 cc. flask supported in a large beaker of cold water. Boil in a small flask for about a minute a mixture of 25 cc. water and 10 cc. 85%  $H_3PO_4$  (to expel any  $CO_2$  present in it). Pour this mixture into the distilling flask with the aid of a small funnel connected with the long, straight tube. Heat the mixture to boiling, distil till about 10 cc. have passed over, and then remove the distillate. (White precipitate, presence of CARBONATE or some SULFUR-CONTAINING CONSTITUENT.)

Cool the distillate and make it slightly acid with HAc. (Complete or partial solution of the precipitate, presence of CARBONATE; residue (S or  $\text{BaSO}_3$ ), presence in the substance of free SULFUR, SULFIDE, SULFITE, or THIOSULFATE.) If there is a residue, treat one-half of the mixture immediately by P. 102, and separate portions of the remainder by P. 103, 104, 105, and 106. If there is no residue, treat separate portions of the whole distillate by P. 103, 104, 105, and 106.

Introduce the end of the delivery tube of the distilling flask into another receiving flask containing 35 cc. water. Continue the distillation until the liquid becomes sirupy, boils more quietly, and begins to give off fine white fumes. Treat this distillate as directed in P. 107.

To the contents of the distilling flask, while still warm, add 5–10 g. of copper filings or turnings. Distil for 3–5 minutes longer, collecting the distillate in 15 cc. of water. Note the odor of the distillate, and treat it by P. 112.

*Notes.*—1. It is necessary to use a Jena-glass flask, since one of ordinary glass is quickly destroyed by the action of hot, concentrated  $\text{H}_3\text{PO}_4$ . The boiling is sometimes violent, especially when much insoluble material is present. The addition of the glass beads serves to reduce the bumping; and placing the flask in an inclined position prevents material from being thrown over into the distillate, which would lead to error in the subsequent tests. In any case in which it seems possible that some of the boiling liquid has been thrown over into the distillate, a small portion of the latter should be tested for phosphate by adding an equal volume of  $(\text{NH}_4)_2\text{MoO}_4$  solution (see P. 115).

2. Phosphoric acid, which is ionized into  $\text{H}^+$  and  $\text{H}_2\text{PO}_4^-$  to a moderate extent (about 27% in 0.1 molal solution), displaces almost completely from their salts (unless these are very difficultly soluble) the much less ionized acids,  $\text{H}_2\text{CO}_3$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{S}$ ,  $\text{HClO}$ ,  $\text{HCN}$ ,  $\text{HF}$ , and  $\text{H}_3\text{BO}_3$ , and also to a large extent the moderately ionized  $\text{H}_2\text{SO}_3$ . Since all these acids, except  $\text{HF}$  and  $\text{H}_3\text{BO}_3$ , volatilize readily out of aqueous solution, they pass over almost or quite completely into the first distillate,  $\text{HClO}$  in the presence of chloride giving  $\text{Cl}_2$ . The largely ionized acids,  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{HSCN}$ ,  $\text{HNO}_3$ ,  $\text{HClO}_3$ ,  $\text{H}_3\text{Fe}(\text{CN})_6$ , and  $\text{H}_4\text{Fe}(\text{CN})_6$ , are not found in any considerable proportion in the first distillate, since they are displaced from their salts much less completely, and since in addition they are much less volatil. Of these the first five pass over unchanged and almost completely into the second distillate; for after the  $\text{H}_3\text{PO}_4$  has become fairly concentrated, the acids are displaced to a greater extent and volatilize more readily in consequence of the higher temperature at which the mixture boils and the smaller proportion of water it contains. From the stronger  $\text{H}_3\text{PO}_4$  solution  $\text{HF}$  also passes over in large quantity; but this is not true of  $\text{H}_3\text{BO}_3$  and  $\text{H}_2\text{SO}_4$ , which volatilize only in insignificant amounts even when the acid has become nearly anhydrous. The three acids,  $\text{HClO}_3$ ,  $\text{H}_4\text{Fe}(\text{CN})_6$ , and  $\text{H}_3\text{Fe}(\text{CN})_6$ , are not volatil as such, but are decomposed by the  $\text{H}_3\text{PO}_4$  after it becomes fairly concentrated— $\text{HClO}_3$  with formation of  $\text{Cl}_2$  and  $\text{HCl}$ ,  $\text{H}_3\text{Fe}(\text{CN})_6$  and  $\text{H}_4\text{Fe}(\text{CN})_6$  with formation of free  $\text{HCN}$ . In regard to the acids that may be present in the two distillates, see also Table X.

3. The barium salts of all the acids passing into the first distillate, except the carbonate and sulfite, remain in solution. Phosphoric acid, if thrown over mechanically, would, however, also give a precipitate. Sulfur, when present in the free state or when liberated from a polysulfide or thiosulfate, volatilizes with the steam, and gives a turbid appearance to the water condensed in the delivery tube and to the barium hydroxide solution, by which it is little acted on in the cold. Chlorine is converted by the barium hydroxide into barium chloride and hypochlorite; bromine, into bromide, hypobromite, and bromate; and iodine, mainly into iodate and iodide.

4. On acidifying the first distillate slightly with HAc,  $\text{BaCO}_3$  dissolves, but  $\text{BaSO}_3$  does not. This difference in behavior is due to the fact that hydrocarbonate-ion ( $\text{HCO}_3^-$ ) is much less ionized than hydrosulfite-ion ( $\text{HSO}_3^-$ ). Sulfur, if present, also remains undissolved. The addition of HAc causes the liberation almost at once of chlorine, bromine, or iodine from a mixture of hypochlorite and chloride, hypobromite and bromide, or iodate and iodide; but bromine is set free somewhat more slowly from a mixture of bromate and bromide.

5. A small precipitate obtained in this procedure (or in the following one) does not prove the presence of carbonate in the mixture unless the prescribed precautions are carefully observed—namely, the boiling of the original  $\text{H}_3\text{PO}_4$  solution, and avoiding the exposure to the air of the various solutions, especially that of the  $\text{BaO}_2\text{H}_2$ . Even with these precautions, however, it is seldom possible to prevent the absorption of enough  $\text{CO}_2$  to produce a slight turbidity.

6. Upon boiling the  $\text{H}_3\text{PO}_4$  with the copper,  $\text{H}_2\text{SO}_4$ , if present, is reduced to  $\text{H}_2\text{SO}_3$ ; and this passes over into the distillate in the form of  $\text{SO}_2$  gas. Less than 1 mg.  $\text{SO}_4$  can be detected by this process of distillation. The copper should be finely divided and should be added while the liquid is still warm, since on cooling it solidifies to a glassy mass, which consists of pyrophosphoric acid ( $\text{H}_4\text{P}_2\text{O}_7$ ). The heating should be continued for 5–10 minutes; but, if much more prolonged, the contents of the flask change to a solid mass, owing to conversion of the pyro to metaphosphoric acid ( $\text{HPO}_3$ ), which can afterwards be removed only with much difficulty.

7. With reference to the analysis of the first and second distillates, provided for in the subsequent procedures, certain facts are to be noted which in many cases greatly reduce the number of these special tests which it is necessary to make. In the first place, some of the acids are incompatible with each other, so that when certain ones are found, others need not be tested for: thus in the acidified distillate  $\text{H}_2\text{S}$  can not be present with  $\text{H}_2\text{SO}_3$ ,  $\text{HNO}_2$ , or free halogen;  $\text{HNO}_2$  and  $\text{H}_2\text{SO}_3$  can not be associated with each other or with free halogen, etc. Secondly, the nature of the basic elements taken in connection with the solubility of the substance often excludes certain acidic constituents; thus in a substance containing barium and soluble in water or very dilute acid, sulfate can not be present; in a water-soluble substance containing silver, none of the acids precipitated by silver nitrate can be present. Thirdly, the general character or known source of the substance may make many of the tests unnecessary; thus, it is useless to test a mineral for nitrite, sulfite, oxyhalogen salts, simple or complex cyanides, oxalate, or other organic salt. The analyst should, therefore, always consider these aspects of the problem, shortening the procedure in such ways as his knowledge makes possible.

TABLE XI.—ANALYSIS OF THE FIRST DISTILLATE.

FIRST DISTILLATE.—Precipitate: $\text{BaCO}_3$ , $\text{BaSO}_3$ , S. Solution: Barium hypohalites (with halides), $\text{Ba}(\text{NO}_2)_2$ , $\text{BaS}$ , $\text{Ba}(\text{CN})_2$ . To the whole mixture add $\text{HAc}$ (P. 101). Precipitate: $\text{BaSO}_3$ , S. Solution: $\text{H}_2\text{CO}_3$ , $\text{Cl}_2$ , $\text{Br}_2$ , $\text{I}_2$ , $\text{HNO}_3$ , $\text{H}_2\text{S}$ , $\text{HCN}$ . Treat portions of the unfiltered mixture as follows:								
Add $\text{HCl}$ and filter (P. 102).			Introduce 1 cc. in- to an inverted tube filled with a solution of $\text{HCl}$ and urea (P. 104).  Gas evolved: $\text{N}_2$ . (Shows NITRITE.)	Filter, add $\text{Cd}(\text{NO}_3)_2$ (P. 105).  Precipitate: $\text{CdS}$ . (Shows SUL- FIDE.)	Treat with $\text{NaOH}$ , $\text{FeSO}_4$ , and $\text{FeCl}_3$ ; boil, add $\text{HCl}$ (P. 106).  Blue precipitate $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$ . (Shows CYANIDE.)			
Residue: S. (Shows SUL- FIDE OR THIOSUL- FATE.)	Solution.	Add $\text{Br}_2$ .				Add $\text{HAc}$ and $\text{CHCl}_3$ (P. 103). (Purple color shows IODIN.) (Orange color shows BROMIN.) Treat portions of the aqueous layer as follows:		
	Precipitate: $\text{BaSO}_4$ .*	Solution: $\text{H}_2\text{CO}_3$ .					If the $\text{CHCl}_3$ was colorless, add $\text{KI}$ and $\text{CHCl}_3$ .	Add $\text{HNO}_3$ , extract with $\text{CHCl}_3$ .  Chloroform layer: $\text{I}_2$ , $\text{Br}_2$ , $\text{Cl}_2$ . Shake with $\text{H}_2\text{SO}_4$ .
	Distil into $\text{Ba}(\text{OH})_2$ .							
	Precipitate: $\text{BaCO}_3$ . (Shows CARBONATE.)							

\* Shows SULFITE OF THIOSULFATE

† The solution is subjected to this treatment only when the previous indications have not led to definite conclusions as to the presence or absence of each of the three halogens

## ANALYSIS OF THE FIRST DISTILLATE.

See Table XI, page 82.

**Procedure 102.**—*Detection of Carbonate and Sulfur-containing Constituents.*—To one-half of the first distillate (P. 101), if there was a residue on adding HAc, add 1–2 cc. HCl. (Residue, presence of free SULFUR, SULFIDE, or THIOSULFATE.) Filter, and add to the filtrate saturated bromin solution till the liquid becomes slightly yellow. (White precipitate, presence of SULFITE or THIOSULFATE.) Transfer the mixture to a distilling apparatus such as is used in P. 101, first filtering out the precipitate if it is large, distil for a minute or two, collecting the vapors in 20 cc. saturated Ba(OH)<sub>2</sub> solution. (White precipitate, presence of CARBONATE.) Acidify slightly with HAc. (Solution of the precipitate, presence of CARBONATE.)

If H<sub>2</sub>SO<sub>3</sub> is found in the distillate, treat a fresh portion of the original substance by P. 118, to determine whether it comes from a sulfite or thiosulfate.

*Notes.*—1. See P. 101, Notes 3–5. Since H<sub>2</sub>SO<sub>3</sub> slowly oxidizes to H<sub>2</sub>SO<sub>4</sub> in the air, the solution should be treated with HCl at once. If any H<sub>2</sub>SO<sub>4</sub> has been formed in this way, it will be precipitated as BaSO<sub>4</sub> before the addition of Br<sub>2</sub>. Care must be taken to add enough Br<sub>2</sub> to complete the oxidation, since otherwise in the subsequent distillation SO<sub>2</sub> will distil over and might be mistaken for carbonate.

2. If there is a large precipitate of BaSO<sub>4</sub>, it is filtered out, since otherwise it is difficult to avoid violent bumping during the distillation. Exposure to the air, and especially to the breath, should, however, be avoided so far as possible, so that CO<sub>2</sub> may not be absorbed from it.

3. A residue of sulfur may arise from the presence in the substance of free sulfur, of a persulfide, of an ordinary sulfide together with some oxidizing substance, or of a thiosulfate.

**Procedure 103.**—*Detection of Nitrite and Free Halogen.*—To one-fourth of the first distillate (P. 101), or of what remains of it (P. 102), add 1–2 cc. HAc and 2–3 cc. of chloroform, and shake vigorously. (Purple coloration of the chloroform, presence in the distillate of free IODIN; yellow or orange coloration, of free BROMIN.)

If there is no coloration, pour about a third of the aqueous layer into a test tube, add 1 cc. chloroform and a few drops 1% KI solution, and let the mixture stand for 5 minutes, noting whether the color due to liberated iodine increases. (Purple color, presence in the distillate of CHLORIN, or, if the color gradually increases, of NITROUS ACID; no color, absence of NITRITE in the substance.)

If there is a coloration after the addition of KI, test a 1 cc. portion of the first distillate (P. 101) for NITRITE by P. 104.

If these tests show the absence of nitrite and the presence of free halogen, but do not warrant definite conclusions as to the presence or absence of each one of the three halogens, proceed as follows: Add 5 cc.  $\text{HNO}_3$  to the remaining two-thirds of the aqueous layer, separate the chloroform from it by means of a separating funnel, shake that layer a second and third time with 3 cc. of fresh chloroform, and separate the layers sharply again. Unite the three portions of chloroform, wash it once in the separating funnel by shaking it with about one-third its volume of  $\text{HNO}_3$ , add the chloroform to an equal volume of  $\text{H}_2\text{SO}_4$  solution in a separating funnel, shake, draw off and reject the chloroform layer, and test the aqueous layer for bromide and chloride by P. 110.

If free halogen is found present in the distillate, test fresh portions of the original substance for hypochlorite by P. 116 and for chlorate by P. 117.

*Notes.*—1. For the reactions between the halogens and barium hydroxide and their re-formation on acidifying with  $\text{HAc}$ , see P. 101, Note 4.

2. The free halogens distribute themselves between the chloroform and water phases. In the case of pure bromin or iodine the ratio of the concentration in the chloroform to that in the water layer is very large and is almost independent of the concentration. This is in accordance with the so-called distribution law, which requires that the ratio of the concentrations of a given molecular species, such as  $\text{Br}_2$  or  $\text{I}_2$ , in the two solvents be constant. When an iodide, like  $\text{HI}$ , is also present, the proportion of iodine extracted by the chloroform is greatly reduced, since the iodine in the aqueous layer is largely combined with the iodide in the form of the triiodide ( $\text{HI}_3$ ); but it is still sufficient to make the color-test a very delicate one.

3. The characteristic purple color given to chloroform is so delicate a test that even 0.05 mg. of iodine in the solution tested can be detected by this procedure. Bromine may be detected, but only in the absence of iodine, by the orange or yellow color of the chloroform layer when not less than 0.5 mg. of bromine is present in the solution tested. (If a few drops of  $\text{KI}$  solution be added to one-third of the chloroform layer, the more intense color of the iodine liberated will enable a smaller quantity of bromine to be detected.) Chlorine gives no decided color to the chloroform, but like bromine causes liberation of iodine on the addition of  $\text{KI}$ . For extracting the halogens from aqueous solutions carbon tetrachloride or carbon bisulfide may be used instead of chloroform; but carbon bisulfide has the disadvantage of being highly inflammable.

4. Nitrous acid, like bromine or chlorine, liberates iodine from  $\text{KI}$ . The reaction is delicate enough to enable 0.1 mg.  $\text{NO}_2$  to be detected in the solution tested. A peculiarity of this reaction is that the nitric oxide which is formed reacts with the iodide, so that a continuous liberation of iodine results. Thus the nitrous acid acts as a catalyzer of the reaction between oxygen and  $\text{HI}$ . This progressive liberation of iodine is highly characteristic of nitrous acid, but renders it difficult to estimate the amount of it present. Since this behavior

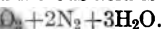
acid, a fresh portion of the distil-

late, it shows the absence of free  
ed by chlorin or bromin very  
during the distillation with phos-

ains a considerable proportion of  
ilibrium conditions of the reaction  
proportion present as  $\text{Cl}_2$  decreases  
and since the  $\text{Cl}_2$  alone dissolves  
extracted from a nitric acid solution  
law, be much larger than  
ever, to extract small amounts of  
add chloride as well as the acid.  
these tests it shows either that the  
in the free state, or (what is  
g the distillation with phosphoric  
oxidizing substance, or from an oxy-  
late, bromate, etc.) by spontaneous  
reducing substances. When free  
of the original substance is there-  
to determin from what source the

If the results of P. 103 show  
 $\text{NO}_3$ , determin its presence or  
with a 20% solution of urea  
containing more of the same  
distillate (P. 101) into the weigh-  
which has one end closed with  
n out and bent so as to form  
e an air-bubble at the same  
(NITRITE.)

and nitrous acid is



bubbles which collect at the top  
it also separates as a gas; but a  
id. The amount of nitrite present  
test with a known quantity of

in the 1 cc. of solution tested to be  
the distillate is used, a more delicate  
er amount of the distillate slightly  
cc., acidify with a drop or two  
the procedure. In this proces  
haline so as to avoid loss of  $\text{HNO}_2$ .  
carbonic acid may be expelled from



They do not do so when dissolved  
they interfere with the test when

soluble in water, this test may extract of the original substance. of the substances present makes completely decomposed during the

To one-half of what still  
add 2-3 cc.  $\text{Cd}(\text{NO}_3)_2$  solution.

detected in the distillate by its weakly acid solution has the advantage to be approximately estimated. solution from any other source,

illate does not prove the absence of the latter has dissolved completely. Soluble sulfides, such as  $\text{CuS}$ , are concentrated, as it does in the ore directed in P. 107 and P. 112 to the sulfide.

Place what remains of the NaOH solution, about 0.5 cc. ( $\text{SO}_4 \cdot 7\text{H}_2\text{O}$ ), and 1 or 2 drops of water. To the hot mixture add a few drops of concentrated HCl. On making, the dark colored precipitate is dissolved. Cool the mixture, filter, and wash out the precipitate. (presence of CYANIDE)

Formation of ferrocyanide by the  
upon the reaction between this  
ferrocyanide (Prussian blue) is  
hydrochloric acid.

in the reddish-yellow colored solution, especially the precipitate on the filter with dilute hydrochloric acid. The test can be detected.

... in the form either  
... are characterized by complex  
(...). These differ very greatly in  
the difference depending on the  
simple ions ( $\text{Ag}^+$  and  $\text{CN}^-$  or

$\text{Fe}^{++}$  and  $\text{CN}^-$ ). Ferrocyanides, ferricyanides, and cobaltcyanides are so slightly dissociated in this way that scarcely any HCN is produced when dilute HCl,  $\text{HNO}_3$ , or  $\text{H}_2\text{SO}_4$  is added to their cold solutions; but almost all the other complex cyanides (such as  $\text{KAg}(\text{CN})_2$  or  $\text{K}_2\text{Ni}(\text{CN})_4$ ) are readily decomposed by these acids.—In the distillation with  $\text{H}_3\text{PO}_4$ , not only the simple cyanides, but also nearly all the complex cyanides are decomposed during the first part of the distillation; but a few very stable substances (such as Prussian blue) are completely decomposed only in the second part of the distillation.

4. The following procedure enables 2 mg. cyanide to be detected in the presence of ferro or ferricyanide: Place in a 20 cc. distilling flask provided with a thistle-tube 0.5–1 g. of the original substance, 2 g. powdered  $\text{CaCO}_3$ , and 10 cc. water. Add very gradually through the thistle-tube 2 cc. HCl (enough to decompose some, but not all of the  $\text{CaCO}_3$ ). Allow the gas which is evolved to pass into a small test-tube containing 1 cc. NaOH and 5 cc. water. Finally heat the contents of the flask almost to boiling. Test the NaOH solution for cyanide by P. 107. This separation depends upon the fact that HCN is displaced by  $\text{H}_2\text{CO}_3$  from simple cyanides and from the relatively unstable complex cyanides, such as  $\text{Ag}(\text{CN})_2^-$  or  $\text{Ni}(\text{CN})_4^{2-}$ , but not from ferro or ferricyanides.

5. Ferrocyanide and ferricyanide may be detected and distinguished from each other when only one of them is present, by adding a ferric salt to one portion of an aqueous or dilute acid solution, and by adding ferrous salt to another portion of the solution. A ferric salt gives a blue precipitate of ferric ferrocyanide with ferrocyanide, but no precipitate with a ferricyanide. A ferrous salt gives the same blue precipitate (of ferric ferrocyanide) with a ferricyanide; but it also gives with a ferrocyanide a precipitate (of ferrous ferrocyanide), which is white if no ferric salt is present, but which rapidly turns blue in contact with the air.

6. Ferrocyanide and ferricyanide may be detected in the presence of each other by proceeding as follows: Add to an aqueous or dilute solution of the substance  $\text{AgNO}_3$  and then a moderate excess of  $\text{NH}_4\text{OH}$ . (White precipitate insoluble in  $\text{NH}_4\text{OH}$ , presence of FERROCYNIDE. Orange to red precipitate readily soluble in  $\text{NH}_4\text{OH}$ , presence of FERRICYANIDE.) Filter out and wash the precipitate, and pour over it a little  $\text{FeCl}_3$  solution. (Blue coloration, presence of FERROCYNIDE.) Acidify the ammoniacal filtrate with HAc, filter out and wash the precipitate, and pour through the filter containing it a little  $\text{FeSO}_4$  solution. (Orange-red precipitate, which is turned blue by the  $\text{FeSO}_4$ , presence of FERRICYANIDE.) This procedure enables 0.2 mg.  $\text{Fe}(\text{CN})_6$  as either ferro or ferricyanide to be detected when present alone; but the test for ferricyanide is much less delicate in the presence of much ferrocyanide.

TABLE XII.—ANALYSIS OF THE SECOND AND THIRD DISTILLATES.

SECOND DISTILLATE: $H_2S$ , $HSCN$ , $HCl$ , $HBr$ , $HI$ , $HNO_3$ . Treat separate portions as follows:					THIRD DISTILLATE:	
If $AgNO_3$ gives a precipitate, treat separate portions as follows:						
Add $AgNO_3$ (P. 107).  Precipitate: $AgCl$ , $AgBr$ , $AgI$ , $AgSCN$ , $Ag_2S$ , $AgCN$ .	Add $Cd(NO_3)_2$ (P. 105).	Add $FeCl_3$ and $HNO_3$ (P. 108).	Add $CHCl_3$ (P. 109).	Distil with $H_2SO_4$ and $FeSO_4$ (P. 111).	$H_2SO_3$ . Add $HCl$ , $BaCl_2$ , and $Br_2$ (P. 112).	
	Precipitate: $CdS$ . (Shows SULFIDE.)	Red color: $Fe(SCN)_2$ . (Shows THIOCYANATE.)	CHCl <sub>3</sub> layer: $I_2$ , $Br_2$ , $Cl_2$ .* If colorless, add $KI$ .			Distillate: $HNO_3$ . Add $KI$ and $CHCl_3$ .
			Purple color: $I_2$ . (Shows CHLORIN.)		Purple color: $I_2$ . (Shows NITRATE.)	
			CHCl <sub>3</sub> layer, purple: $I_2$ . (Shows IODIDE.)			Water layer. Add $H_2SO_4$ and more $KMnO_4$ and $CHCl_3$ .
			CHCl <sub>3</sub> layer, orange: $Br_2$ . (Shows BROMIDE.)			Water layer. Boil to expel $Br_2$ , filter, add $H_2SO_3$ , $HNO_3$ and $AgNO_3$ .
Precipitate: $AgCl$ . (Shows CHLORIDE.)						

\* Purple coloration shows iodine, orange coloration, bromine.

## ANALYSIS OF THE SECOND AND THIRD DISTILLATES.

See Table XII, page 88.

**Procedure 107.**—*Detection of Constituents Precipitable by Silver Nitrate.*—To one-eighth of the second distillate add 1 cc.  $\text{HNO}_3$  and 1 cc.  $\text{AgNO}_3$  solution. (White precipitate, presence of CHLORIDE, CYANIDE, or THIOCYANATE; yellowish precipitate, presence of BROMIDE or IODIDE; black precipitate, presence of SULFIDE; no precipitate, absence of all these in this distillate.)

If there is a precipitate, test one-sixth of the second distillate for sulfide by P. 105 (see, however, Note 2), and another sixth for thiocyanate by P. 108; and then test the remainder for free halogen and halides by P. 109 and 110, and for nitrate by P. 111.

If there is no precipitate, test the distillate for nitrate by P. 111.

*Notes.*—1. All the common silver salts, except the halides, cyanide, thiocyanate, and sulfide are either soluble in water (as are the nitrate, sulfate, chlorate, and fluoride), or dissolve readily in  $\text{HNO}_3$  owing to displacement of the weaker acid (as do the phosphate, carbonate, borate, and sulfite). It should be noted, however, that salts of weak acids are not necessarily readily soluble in a strong acid. Thus  $\text{Ag}_2\text{S}$  does not dissolve in dilute  $\text{HNO}_3$  because its solubility in pure water is so extremely small that there is only a very minute concentration of  $\text{S}^{2-}$  ion in the saturated solution, and this can yield, in accordance with the mass-action law, only a relatively small concentration of  $\text{SH}^-$  and unionized  $\text{H}_2\text{S}$  with the  $\text{H}^+$  ion of the  $\text{HNO}_3$ . Silver cyanide has for another reason a very slight concentration of its anion in its saturated solution; namely, because of the fact that this salt exists in the solution mainly as  $\text{Ag}^+$  and  $\text{Ag}(\text{CN})_2^-$ , and scarcely at all as  $\text{Ag}^+$  and  $\text{CN}^-$ .

2. It is not necessary to test for cyanide in this distillate; for even the insoluble ferro and ferricyanides are decomposed partly, tho not necessarily completely, in the first part of the distillation. It is, however, advisable to test for sulfide unless the substance dissolved completely in the hot dilute  $\text{H}_3\text{PO}_4$ , or unless the  $\text{AgNO}_3$  precipitate is pure white. For some insoluble sulfides begin to decompose only when the  $\text{H}_3\text{PO}_4$  becomes concentrated.

**Procedure 108.**—*Detection of Thiocyanate.*—If  $\text{AgNO}_3$  produced a precipitate (P. 107), dilute a sixth of the second distillate (P. 101) to 5–10 cc., add 2–3 drops of  $\text{FeCl}_3$  solution and 2–3 drops of  $\text{HCl}$ . (Red color, presence of THIOCYANATE.)

*Notes.*—1. The red coloration arises from the formation by metathesis of  $\text{Fe}(\text{SCN})_3$ , a substance whose degree of ionization is relatively small. The  $\text{HCl}$  is added to reduce the hydrolysis of the  $\text{FeCl}_3$  and diminish the color imparted by it to the solution.—A distinct reddish-yellow coloration is produced by 0.1 mg.  $\text{SCN}$ . A deep red color is obtained when 1 mg. or more is present.

2. Since in the distillation with  $\text{H}_3\text{PO}_4$ , thiocyanates are destroyed by certain oxidizing agents, such as nitrates, which do not act on it at ordinary temperatures, it is sometimes advisable to apply this test also to a solution of the original substance.

**Procedure 109.**—*Detection and Removal of Free Halogens.*—If  $\text{AgNO}_3$  gave a precipitate in P. 107, to three-fourths of the remainder of the second distillate in a separating funnel add 2–3 cc. chloroform and shake. (Purple color, presence of IODIN; orange or yellow color, presence of BROMIN.)

If the chloroform is colorless, separate it from the aqueous layer. Add to the chloroform layer a few drops of KI solution. (Purple color, presence of CHLORIN, or of BROMIN in small quantity.) If there is no color, treat the aqueous layer left in the separating funnel by P. 110.

If any free halogen is present, add to the mixture in the separating funnel 10 cc. chloroform, shake, and separate the two layers. Repeat the extraction with a fresh 10 cc. portion of chloroform. (Purple color of the chloroform layer and brown color of the aqueous layer, showing slow extraction of iodine, presence of IODIDE.) Test the aqueous layers for halides by P. 110.

If further tests for free bromine or chlorine are necessary, shake the chloroform extracts with 10 cc. water, adding enough  $\text{H}_2\text{SO}_3$  solution to reduce the halogen, and treat the aqueous layer by P. 110.

*Notes.*—1. As to these tests see the notes to P. 103.

2. As there stated, the proportion of the iodine extracted from the aqueous layer by chloroform is much smaller when iodide is also present, so that some tri-iodide then remains in the aqueous solution after two extractions. Since this behavior itself shows the presence of iodide, it is not necessary to attempt to extract all the iodine before testing for halides by P. 110.

**Procedure 110.**—*Detection of Halides.*—Place the aqueous layer which is to be tested for halides (P. 109) in a separating funnel; add 3 cc. chloroform, 8 cc. normal sodium acetate solution, 2 cc. HAc, and 1 cc. 1%  $\text{KMnO}_4$  solution (in excess of that required to oxidize any  $\text{H}_2\text{SO}_3$  present), and shake. (Purple color, presence of IODIDE.) If there is a color, pour the mixture into a flask, add 10 cc. more  $\text{CHCl}_3$ , and then add gradually 1%  $\text{KMnO}_4$  solution, shaking after each addition, till the aqueous layer becomes pink. Pour the mixture through a moistened filter to remove the chloroform and precipitated  $\text{MnO}_2$ , and shake the filtrate once or twice with a fresh 10 cc. portion of chloroform to extract all the iodine.

Place the aqueous solution and 3 cc. chloroform in a separating funnel, add 5 cc.  $\text{H}_2\text{SO}_4$ , and 1 cc. 1%  $\text{KMnO}_4$  solution, unless such an excess is already present, and shake. (Yellow or orange coloration of the chloroform, presence of BROMIDE.)

Transfer the aqueous layer to a casserole, add 5–20 cc. 1 %  $\text{KMnO}_4$  solution, and boil the mixture 3–5 minutes, or until the volume has been reduced to 10 cc. Filter off the  $\text{MnO}_2$ , and, if the solution is still pink, add  $\text{H}_2\text{SO}_4$  solution drop by drop until it is colorless. Dilute the solution to 100 cc., filter if necessary, and add 2 cc.  $\text{HNO}_3$  and 1–2 cc.  $\text{AgNO}_3$  solution. (White precipitate, presence of CHLORIDE.)

*Notes.*—1. This separation is based upon the different rates at which  $\text{KMnO}_4$  sets free by oxidation the three halogens from their salts in a solution of definite hydrogen-ion ( $\text{H}^+$ ) concentration. A dilute solution of acetic acid containing considerable sodium acetate has such a hydrogen-ion concentration that an iodide is immediately oxidized by  $\text{KMnO}_4$  with liberation of iodine, while bromide and chloride are not oxidized to an appreciable extent in the time required for the operations. When the  $\text{H}^+$  concentration is increased by the addition of the prescribed quantity of  $\text{H}_2\text{SO}_4$ , the bromide is oxidized very rapidly while the rate of the corresponding reaction for the chloride is still so small at room temperature that scarcely any chlorine is set free. Even when the solution is boiled to expel the bromine, only a small fraction of the chloride present is oxidized to chlorine.

2. To secure satisfactory results, the directions as to the quantities of the acids added must be followed carefully. The proper quantity of  $\text{H}_2\text{SO}_4$  is that required to react with all the sodium acetate and to give in addition an excess equal to about 1 cc.  $\text{H}_2\text{SO}_4$  per 20 cc. of solution.

3. A very small precipitate of  $\text{AgCl}$  obtained at the end of the procedure does not necessarily indicate the presence of chloride in the substance, unless the reagents used have been proved to be entirely free from chloride. Even then a very slight precipitate (corresponding to less than 0.1 mg.  $\text{Cl}$ ) may result from a reaction between the permanganate and chloroform. For these reasons a blank test should be made in any doubtful case.

4. The yellow color of bromine in 3–5 cc. chloroform enables about 0.5 mg.  $\text{Br}$  to be detected in this procedure, which corresponds to about 1 mg.  $\text{Br}$  in the whole of the second distillate.

5. If  $\text{HCN}$ ,  $\text{H}_2\text{S}$ , or  $\text{HSCN}$  are present in the distillate, they will be expelled or destroyed by the boiling with  $\text{KMnO}_4$  before the final test for chloride with  $\text{AgNO}_3$  is applied.

**Procedure III.—Detection of Nitrate.**—To the remainder of the second distillate (after removing any iodide or thiocyanate present by shaking with solid  $\text{Ag}_2\text{SO}_4$  and filtering) add 3 cc.  $\text{H}_2\text{SO}_4$  (s.g., 1.84) and 5 cc. saturated  $\text{FeSO}_4$  solution. Place the mixture in the apparatus used in P. 101, and distil until only about 5 cc. remain, collecting the distillate in a mixture of 20 cc. water and 1 cc.  $\text{NaOH}$  solution. Make the distillate acid with  $\text{H}_2\text{SO}_4$ , add 2–3 cc. chloroform, and shake (to make sure that the chloroform remains colorless). Then add a few drops of  $\text{KI}$  solution, and shake again. (Purple color, presence of NITRATE.)

*Notes.*—1. In this procedure the nitrate is reduced by the  $\text{FeSO}_4$  to nitric oxide ( $\text{NO}$ ), which passes over as a gas into the receiver, where it is oxidized by the oxygen of the air to  $\text{HNO}_2$ , which is then absorbed by the  $\text{NaOH}$ . When the solution is acidified and  $\text{KI}$  added,  $\text{I}_2$  is liberated by the  $\text{HNO}_2$  (see P. 103, Note 4). By this procedure 0.2 mg.  $\text{NO}_3$  in the liquid submitted to distillation can be detected.

2. The reaction is highly characteristic for nitrates, since any nitrous acid present passed over completely into the first distillate, and since other oxidizing substances (for example, chlorine or bromine) which might liberate iodine from potassium iodide are reduced by the  $\text{FeSO}_4$  to compounds which, even if they pass over into the distillate, have no action on  $\text{KI}$ . The only substances that may interfere are iodide and thiocyanate; and provision is therefore made for first removing these by adding solid  $\text{Ag}_2\text{SO}_4$ , shaking, and filtering.

**Procedure 112.—Detection of Sulfate.**—To the third distillate obtained upon heating with copper (P. 101), add 1–2 cc.  $\text{HCl}$ , 3–5 cc.  $\text{BaCl}_2$  solution, and saturated  $\text{Br}_2$  solution till the liquid becomes yellow. (White precipitate, presence of **SULFATE**.)

*Notes.*—1. By the action of copper in the presence of concentrated  $\text{H}_3\text{PO}_4$  on sulfates (even on the very difficultly soluble  $\text{BaSO}_4$ )  $\text{SO}_2$  is formed. This is oxidized by the  $\text{Br}_2$  to  $\text{H}_2\text{SO}_4$ , which then precipitates as  $\text{BaSO}_4$ . In this way 1 mg.  $\text{SO}_4$  may be detected. Even when this small amount is present in the substance, only an inconsiderable proportion of it passes into the first and second distillates.

2. Much  $\text{H}_3\text{PO}_4$  also passes over into the distillate; and the  $\text{HCl}$  is added to prevent its precipitation as  $\text{BaHPO}_4$ . Too much  $\text{HCl}$  must not be added since  $\text{BaSO}_4$  is appreciably soluble in it.

3. When a sulfide is present which has not already been decomposed, sulfur and  $\text{H}_2\text{S}$  may pass into the third distillate, after the acid has become concentrated. The  $\text{H}_2\text{S}$  may be tested for in a portion of the distillate by P. 105.

TABLE XIII.—SUPPLEMENTARY PROCEDURES.

Treat portions of the original substance as follows:

Distill with $\text{CH}_3\text{OH}$ and $\text{H}_2\text{SO}_4$ (P. 113).	Heat with $\text{SiO}_2$ and $\text{KHSO}_4$ (P. 114).	Boil with $\text{HNO}_3$ , add $(\text{NH}_4)_2\text{MoO}_4$ (P. 115).	*Heat with water, $\text{HAc}$ , and $\text{PbAc}_2$ (P. 116).	*Add dilute $\text{HNO}_3$ , $\text{Na}_3\text{AsO}_3$ (to reduce hypo- chlorite), and $\text{AgNO}_3$ (P. 117).	† Add $\text{Na}_2\text{CO}_3$ solution and filter; to fil- trate add $\text{Sr}(\text{NO}_3)_2$ and $\text{HAc}$ (P. 118).	‡ Fuse with $\text{Na}_2\text{CO}_3$ , ex- tract with water, filter (P. 119); acidify the filtrate, test portions for chloride, sul- fate, borate, fluoride, phosphate, and silicate.
Distillate: $\text{B}(\text{OCH}_3)_3$ . Collect in $\text{CH}_3\text{OH}$ and $\text{HCl}$ , and add turmeric.	Gases evolved: $\text{SiF}_4$ and $\text{H}_2\text{O}$ . Deposit on cold part of tube: $\text{SiO}_3\text{H}_2$ . (Shows FLUORIDE.)	Yellow precipitate: $(\text{NH}_4)_3\text{PO}_4$ . $12\text{MoO}_3$ . (Shows PHOSPHATE.)	Dark brown precipitate: $\text{PbO}_2$ . (Shows HYPOCHLO- RITE.)	Precipitate: $\text{AgCl}$ , etc. Rejed. Filtrate: $\text{AgClO}_3$ . Add $\text{H}_2\text{SO}_3$ . Precipitate: $\text{AgCl}$ . (Shows CHLORATE.)	Precipitate: $\text{SrSO}_4$ , $\text{SrSO}_3$ . Treat with $\text{HCl}$ , add $\text{BaCl}_2$ . Filtrate: $\text{SrSO}_3$ . Add $\text{HCl}$ and heat. Precipitate: $\text{BaSO}_4$ . Filtrate: $\text{H}_2\text{SO}_3$ . Add $\text{Br}_2$ . Precipitate: $\text{BaSO}_4$ . (Shows SULFITE.)	

\* These tests are made when free halogen was found in the first or second distillate.

† These tests are made when  $\text{H}_2\text{SO}_4$  was found in the first distillate.

‡ These tests are made only when the substance is not completely decomposed by hot concentrated acids.



## SUPPLEMENTARY PROCEDURES.

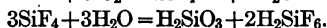
See Table XIII, page 93.

**Procedure 113.**—*Detection of Borate.*—Place 1–2 g. of the finely powdered substance in the distilling apparatus used in P. 101, and add 10 cc. of methyl alcohol ( $\text{CH}_3\text{OH}$ ) and two or three glass beads. Pour in carefully 3 cc.  $\text{H}_2\text{SO}_4$  (s.g., 1.84), and distil off the alcohol, collecting it in a mixture of 5 cc.  $\text{CH}_3\text{OH}$  and 3 cc.  $\text{HCl}$  (s.g., 1.20). Make the distillate up to 18 cc. with  $\text{CH}_3\text{OH}$ , cool, and add five drops of a saturated solution of turmeric in ethyl alcohol. (Red or orange color, presence of BORATE.)

*Note.*—Methyl alcohol reacts with boric acid to form its methyl ester  $\text{B}(\text{OCH}_3)$  which is a readily volatil liquid. The color given by turmeric to a solution of boric acid in methyl alcohol and strong hydrochloric acid is so intense that the test is very delicate if the proportions given are reproduced. The presence of 1 mg.  $\text{BO}_2$  in the substance distilled may readily be detected. To estimate roughly the quantity present, the color may be compared with that given by adding the turmeric solution to known quantities of borate dissolved in a mixture of 3 cc.  $\text{HCl}$  (s.g., 1.20) and 15 cc.  $\text{CH}_3\text{OH}$ .

**Procedure 114.**—*Detection of Fluoride.*—Mix 0.2 g. of the dry, finely powdered substance with twice its weight of powdered  $\text{KHSO}_4$  and with 10–20 mg. dry, finely powdered or precipitated  $\text{SiO}_2$ . Blow a thick-walled bulb  $1\frac{1}{2}$ –2 cm. in diameter at the end of a glass tube of 5–8 mm. bore. Place the mixture in the bulb (not using more of it than will one-third fill the bulb). Heat the bulb carefully until the  $\text{KHSO}_4$  is melted, taking care that the mixture does not froth up into the tube. Continue to heat the bulb and the lower part of the tube until there is a deposit of a solid substance or of condensed acid 3 or 4 cm. above the bulb. After it has cooled, cut off the tube close to the bulb. Dip the tube several times in water, dry it in a flame, and heat it strongly. (White deposit in the middle part of the tube and etched surface at the lower end, presence of FLUORIDE.)

*Notes.*—1. This test depends on the following reactions:



Some of the  $\text{HF}$  liberated by the molten  $\text{KHSO}_4$  volatilizes and takes the silica required for the first reaction from the glass, thus producing the characteristic etched surface in the lower part of the tube. The  $\text{SiF}_4$  gas and the water vapor liberated react in the cooler part of the tube according to the second equation (forming a white ring of solid silicic acid and fluosilicic acid,  $\text{H}_2\text{SiF}_6$ ). The reaction is reversed at higher temperatures, so that the deposit may be driven up the tube by heating. This white deposit is the most characteristic part of the test for fluoride. A deposit of  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  may also form in the upper part of the tube, and might be mistaken for, or interfere with, the test

for small amounts of fluoride, if the final washing with water is omitted. This procedure enables 0.5 mg. F to be easily detected.

2. The test fails with certain minerals which are not decomposed by fusion with  $\text{KHSO}_4$ . Such cases are provided for by the treatment described in P. 119.

3. In distilling a fluoride with  $\text{H}_3\text{PO}_4$  by P. 101, much of the HF reacts with the glass, but enough of it passes into the second distillate to enable 2–3 mg. F in the substance to be detected, if the whole distillate be tested with NaAc and  $\text{CaCl}_2$  as described in P. 119.

4. Fluoride is often tested for by heating the solid substance in a platinum crucible with  $\text{H}_2\text{SO}_4$  alone and detecting any HF evolved by its etching action on a watch glass coated with wax through which markings have been made. This test has the disadvantage that in the presence of silica or silicate, which is very often present in minerals, it is unreliable owing to the conversion of the HF to  $\text{SiF}_4$  by the reaction given in Note 1.

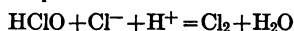
**Procedure 115.—Detection of Phosphate.**—To 0.1–0.2 g. of the finely powdered substance add about 5 cc.  $\text{HNO}_3$ . If the substance does not dissolve, boil the mixture for 2 or 3 minutes, and filter. Add to the filtrate an equal volume of  $(\text{NH}_4)_2\text{MoO}_4$  solution, and allow it to stand 5 to 10 minutes. (Yellow precipitate, presence of PHOSPHATE.)

*Notes.*—1. The yellow precipitate produced is a complex compound, ammonium phosphomolybdate, of a composition varying somewhat with the conditions, but approximating that required by the formula  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ .

2. In order that the test may be delicate, a large proportion of the  $(\text{NH}_4)_2\text{MoO}_4$  must be present to reduce the solubility of the precipitate; and a short time must be allowed for the formation of the complex phosphomolybdate. This is promoted by gentle warming; but in a hot solution arsenate or silicate may give rise to a similar yellow precipitate, while in the cold the reaction is given only by phosphate. By this test 0.1 mg.  $\text{PO}_4$  may be easily detected. The great delicacy of this test should be borne in mind in estimating the quantity of phosphate present.

**Procedure 116.—Detection of Hypochlorite.**—If free halogen was found (in P. 103) to be present in the first distillate, treat 0.5 g. of the powdered substance mixed with 5 cc. water, or 5 cc. of the alkaline solution, as follows: Add HAc, a few drops at a time, until the solution is acid. Filter if there is much residue; add 2–3 cc.  $\text{PbAc}_2$  solution, heat the mixture to boiling, and let it stand for ten minutes. (Brown precipitate, presence of HYPOCHLORITE.)

*Notes.*—1. Hypochlorites are commonly met with either in alkaline solution or in the form of a powder (for example, in bleaching powder). Since they are prepared by the action of chlorine on alkali, chloride is ordinarily present in nearly equivalent amount. When the solid powder is treated with water, the hypochlorite passes into solution; and from it the unionized  $\text{HClO}$  is liberated upon the addition of the more largely ionized acetic acid. Chlorine is also formed until the equilibrium-conditions of the reaction



are satisfied. When in neutralizing with HAc litmus paper is used, the paper will soon be bleached if hypochlorite is present; but the color at the first instant or on the edges of the bleached portion can usually be observed.

2. This test depends upon the oxidation of the lead salt to lead dioxide ( $\text{PbO}_2$ ) by the hypochlorite. The reaction takes place so slowly in the cold that not less than 10 mg.  $\text{ClO}$  in 5 cc. solution can be detected at room temperature, even if the mixture be allowed to stand a few minutes. But when the mixture is heated the limit of detectability is about 0.5 mg. in 5 cc. The solution is acidified with HAc, since oxidation does not take place in the presence of a strong acid, such as  $\text{HNO}_3$ .

3. Peroxides in alkaline solution react instantaneously with lead salts, forming  $\text{PbO}_2$ ; but this reaction does not take place in the presence of HAc, even on boiling. Therefore in the above procedure a peroxide will not be mistaken for a hypochlorite. Peroxide and hypochlorite, moreover, cannot exist together, since they react very rapidly with formation of oxygen.

4. This test for hypochlorite may be made even more delicately in alkaline solution, provided peroxides are known to be absent. If the solution is only slightly alkaline, a small white precipitate of  $\text{Pb}(\text{OH})_2$  or  $\text{PbCO}_3$  is first formed; but this turns brown if hypochlorite is present when the mixture is heated and allowed to stand. The delicacy is of course diminished by the presence of a large amount of  $\text{Pb}(\text{OH})_2$  or  $\text{PbCO}_3$ ; but 1 mg.  $\text{ClO}$  can be detected in the presence of even 2 or 3 g. of these substances, provided an excess of the lead salt is still present in the solution and the mixture is boiled vigorously, preferably in a casserole.

5. Hypobromite in alkaline solution or bromin in HAc solution also oxidizes lead salts to  $\text{PbO}_2$ . Hypobromite is, however, so unstable that it will not be met with except in a solution freshly prepared from bromin and alkali. In a doubtful case the halogens may be extracted by chloroform from an acid solution, and tested for by P. 109 and 110.

**Procedure 117.—Detection of Chlorate.**—If free halogen was found (in P. 103 or P. 109) to be present in the first or second distillate, treat 0.5 g. of the substance in the cold with 50 cc. water and 10 cc.  $\text{HNO}_3$ . (If hypochlorite is present as shown by P. 116, reduce it by adding  $\text{Na}_3\text{AsO}_3$  solution in excess.) Add  $\text{AgNO}_3$  solution as long as a precipitate forms and then about 5 cc. more. Shake the mixture and filter off the precipitate. To the filtrate add 5 cc. saturated  $\text{SO}_2$  solution, heat the mixture, or allow it to stand five minutes. (White precipitate, presence of **CHLORATE** (or **BROMATE**).)

**Notes.**—1. In this procedure chlorate is reduced to chloride by the  $\text{H}_2\text{SO}_3$ . The reaction is not instantaneous; but it is so rapid in the presence of a large excess of  $\text{H}_2\text{SO}_3$  that at room temperature 1 mg.  $\text{ClO}_3$  gives a distinct precipitate of  $\text{AgCl}$  within 5 minutes, even in a volume of 100 cc.

2. If iodate is present,  $\text{AgIO}_3$  is precipitated upon the first addition of  $\text{AgNO}_3$ , along with the silver halides; but if bromate is present, some of it remains in the solution and shows the same behavior as chlorate. If necessary to distinguish between them, the final precipitate with  $\text{AgNO}_3$  may be treated as follows: Suspend it in 25 cc. water, pass in  $\text{H}_2\text{S}$  until the mixture is satu-

rated with it, heat to boiling, filter off the precipitated  $\text{Ag}_2\text{S}$ , boil the filtrate till the  $\text{H}_2\text{S}$  is expelled, and test it for bromide and chloride by P. 110.

**Procedure 118.**—*Detection of Sulfite and Thiosulfate.*—If in P. 102 the first distillate was found to contain  $\text{H}_2\text{SO}_3$ , add 0.5 g. of the finely powdered original substance to 5 cc. water and 1–5 cc.  $\text{Na}_2\text{CO}_3$  solution, shake the mixture, filter out any precipitate or residue, and add to the solution 3 cc.  $\text{Sr}(\text{NO}_3)_2$  solution. Then at once add  $\text{HAc}$  slowly, at the last a few drops at a time, until the precipitate of  $\text{SrCO}_3$  dissolves on shaking, or until the solution reacts acid to litmus. Heat the mixture to boiling, add a drop or two of  $\text{HAc}$  if a flocculent precipitate forms, and let the mixture stand 15 minutes. (No precipitate, absence of SULFITE.)

Filter out the  $\text{Sr}(\text{NO}_3)_2$  precipitate, wash it once with a little cold water, pour a portion of 3–4 cc.  $\text{HCl}$  two or three times through the filter, and add to the solution 5 cc.  $\text{BaCl}_2$  solution. (If a precipitate of  $\text{BaSO}_4$  forms, filter it out.) Then add to the solution saturated  $\text{Br}_2$  solution till the liquid is slightly yellow. (Precipitate, presence of SULFITE.)

To the filtrate from the  $\text{Sr}(\text{NO}_3)_2$  precipitate, add 1–2 cc.  $\text{HCl}$  (s.g., 1.20), heat the mixture to boiling, and let it stand overnight. (White turbidity or yellow precipitate, presence of THIOSULFATE.)

*Notes.*—1.  $\text{Na}_2\text{CO}_3$  is added at the beginning of this procedure to separate from the acidic constituents in question any basic constituents that may be present. All the basic constituents, except arsenic, potassium, sodium, and ammonium, are precipitated by it from solutions of their salts, and most of their slightly soluble compounds are metathesized by it; thus  $\text{BaSO}_3$  is converted into  $\text{BaCO}_3$ . In some systems of analysis most of the acidic constituents are tested for in a solution prepared by boiling the solid substance with  $\text{Na}_2\text{CO}_3$  solution, filtering, and neutralizing the filtrate.

2. The addition of the  $\text{Na}_2\text{CO}_3$  solution and the subsequent neutralization of it by  $\text{HAc}$  also serve to give a solution of small  $\text{H}^+$  concentration, which is essential for a satisfactory separation of sulfite and thiosulfate. When the  $\text{H}^+$  concentration is large,  $\text{SrSO}_3$  dissolves and the thiosulfate decomposes with formation of sulfur; but in  $\text{HAc}$  solution the latter reaction is negligible, even on heating in the presence of a considerable excess of the acid.  $\text{SrSO}_3$  separates as a crystalline precipitate, slowly in the cold when present in small quantity, but much more rapidly when the mixture is heated. The procedure enables 1 mg.  $\text{SO}_3$  in an initial volume of 10 cc. to be easily detected.

3. Upon the addition of a moderate excess of  $\text{HCl}$  over that required to react with all the  $\text{NaAc}$  present, the thiosulfate decomposes with the separation of sulfur. When 10 cc. of solution are treated by the above procedure, a precipitate forms within 30 minutes with 3 mg.  $\text{S}_2\text{O}_3$ , and on standing over night with 1 mg.  $\text{S}_2\text{O}_3$ .

**Procedure 119.**—*Detection of the Acidic Constituents in Undecomposed Substances.*—If the substance is not completely decomposed by acids (as shown in P. 101 and 115) heat 1 g. of the finely powdered substance with  $\text{HNO}_3$ , filter out and wash the residue, dry it, separate from the filter, and mix it with 5–10 g. dry  $\text{Na}_2\text{CO}_3$  in a platinum crucible (or in a porcelain crucible, if reducible metals may be present in it.) Cover the crucible and heat it over a powerful burner for 5–10 minutes. If a perfectly clear fusion does not result, add more  $\text{Na}_2\text{CO}_3$ , and heat again. Cool, place the crucible in a casserole, boil it with water till the fused mass is disintegrated, and filter, rejecting the residue.

To a portion of the filtrate add  $\text{HNO}_3$  till it is distinctly acid, and test portions of the solution for CHLORIDE by adding  $\text{AgNO}_3$ , for PHOSPHATE by P. 115, and for SULFATE by adding  $\text{BaCl}_2$  solution.

Test another portion of the filtrate for BORATE by evaporating it to complete dryness, adding  $\text{H}_2\text{SO}_4$  (s.g., 1.84) drop by drop, and treating the mixture by P. 113.

Test a third portion of the filtrate for FLUORIDE as follows: add 5–10 cc.  $\text{NaAc}$  solution and 5 cc.  $\text{CaCl}_2$  solution, and allow the mixture to stand 10–15 minutes. (White precipitate, presence of FLUORIDE.) To confirm its presence, filter out, wash, and dry the precipitate, and test it by P. 114.

If silicate needs to be tested for, evaporate a portion of the solution, heat the residue at  $100\text{--}125^\circ$  till it is perfectly dry, add  $\text{HCl}$ , and boil gently. (White residue, presence of SILICATE or SILICA.) To confirm its presence, treat the residue by P. 5.

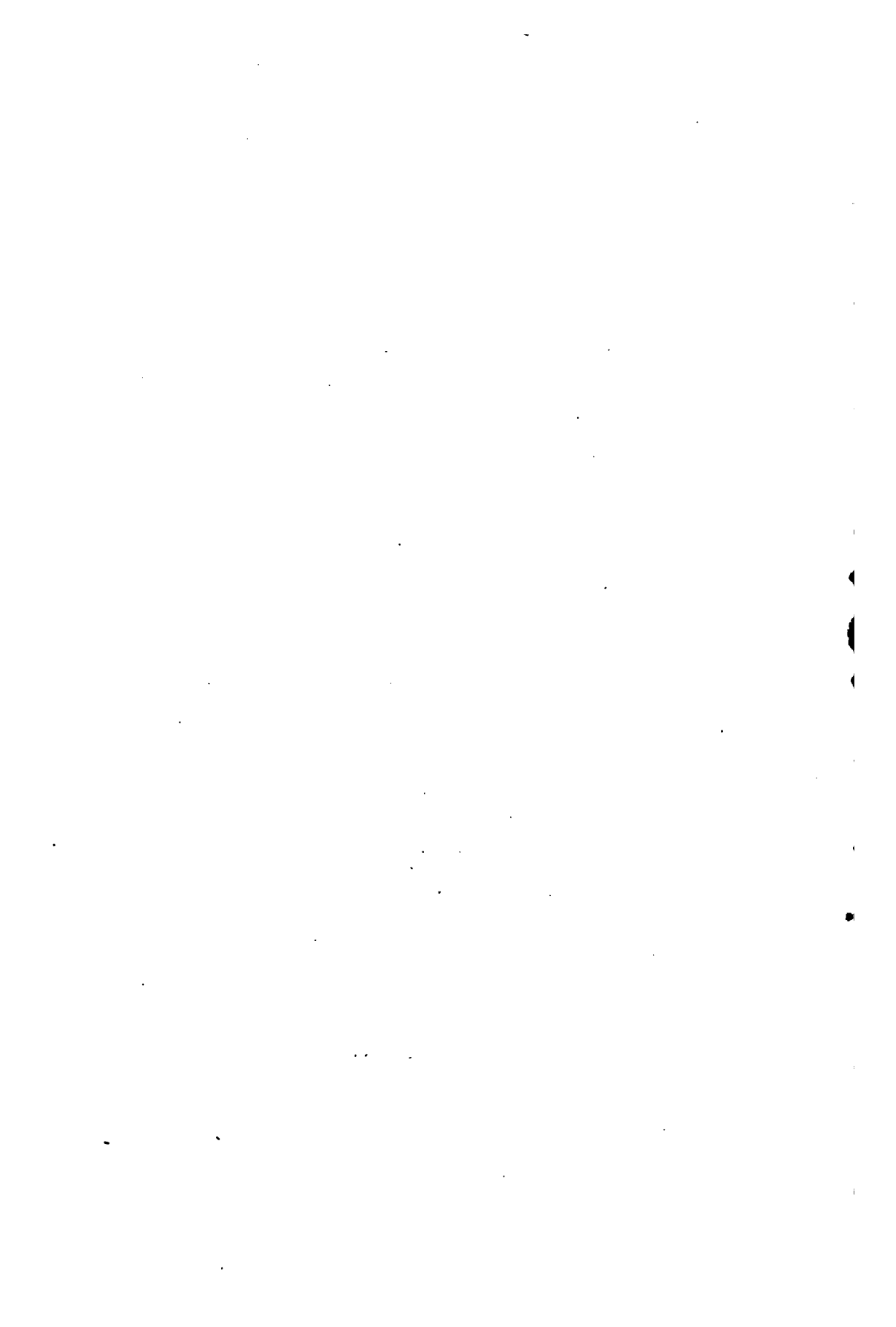
*Notes.*—1. Fusion with  $\text{Na}_2\text{CO}_3$  metathesizes nearly all insoluble compounds in the way described in the notes to P. 7.

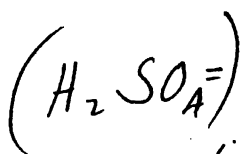
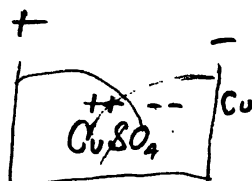
2. If basic elements that may be reduced to the metallic state (those of the silver, copper, and tin groups) may be present in the insoluble residue, it must be fused in a porcelain instead of a platinum crucible. It is, however, less desirable to use a porcelain crucible, since it is more difficult to attain the high temperature necessary, and since it is attacked by the flux and silicate is thereby introduced into the solution.

3. In minerals or metallurgical products undecomposed by acids, it is usually necessary to test only for silicate, chloride, sulfate, phosphate, borate, and fluoride, since other acidic constituents are scarcely ever present.

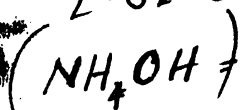
4. The formation of a precipitate in a solution acidified with  $\text{HAc}$  distinguishes fluoride from all other acidic constituents except sulfate and oxalate. The test is delicate enough to enable 0.2 mg. F in 10 cc. solution to be detected.

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